THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 2 DECEMBER, 1934 NUMBER 12

Combination-Scattering and "Association of Molecules"

(Preliminary note)

S. I. LEITMAN AND S. A. UKHOLIN, *Optical Laboratory, Inst. of Physics, University of Moscow*

(Received September 4, 1934)

The molecular association of polar liquids was studied by the combination-scattering (Raman-spectra) method. In the spectra of a water solution of acetic acid the lines corresponding to the wave number 623 cm^{-1} changed their relative intensity at a change of the concentration of solution. This wave number is therefore characteristic of acetic acid complex molecules. No associative lines were observed in the combination spectra of nitrobenzol solution in CCl_4.

SOON after the discovery of the phenomenon of combination-scattering of light, attempts were made to connect certain facts observed in combination spectra with the molecular association of the substance (Meyer,[1] Ganesan and Venkateswaran,[2] Prinsheim and Schlivitch,[3] Dadieu and Kohlrausch,[4] and others). In fact, the combination spectra offer a suitable method for studying the phenomenon of association; when comparing the combination spectra of any substance taken in two different conditions and containing either single molecules or a considerable number of associated molecules, the following may be expected: (1) characteristic frequencies of a single molecule may be somewhat displaced because of the influences exercised on various parts of the molecule by the adjacent molecules; (2) There may be frequencies which are observed only in the presence of associated molecules, and disappear at the same time with the latter. These frequencies may be considered the result of vibration of one part of the associated molecule relative to the other. The existence of such a pronounced frequency is possible, of course, only in cases when there are perfectly definite configurations of associated molecules with quite definite powers interacting between their parts. Otherwise, only diffuse bands may be expected to appear in the combination spectrum. The absence of clearly expressed association lines does not yet solve the question one way or another, but the appearance of such lines may be considered a reliable and suitable indication enabling one to judge of the nature of the new formations. The above-mentioned method of studying the association is convenient because it allows us to observe the effect which is completely connected with the existence of associated molecules and entirely independent of single ones.

The aim of the present work is to study the problem of the existence of associative frequencies characteristic of the substance. It is possible to distinguish the associative frequencies from the insufficiently deciphered combination spec-

[1] Meyer, Phys. Zeits. **30**, 170 (1929), **32**, 293 (1931).
[2] Ganesan and Venkateswaran, Ind. J. Phys. **4**, 195 (1929).
[3] Prinsheim and Schlivitch, Zeits. f. Physik **60**, 582 (1930).
[4] Dadieu and Kohlrausch, Phys. Zeits. **31**, 514 (1930).

trum of the majority of organic matter only by modification of the intensity of certain combination lines, as compared with the others, at a change of temperature or of the concentration of the given liquid in solution. In this work we confined ourselves to the modification of the concentration of the liquid in solution under investigation. As objects of study, nitrobenzol and acetic acid were used, both possessing considerable polar moments and giving noticeable association. CCl_4 was used as a solvent for nitro-benzol, and water for acetic acid. The installation was mounted according to Wood's scheme, with a vertical vessel and a lamp and a prism of total reflection. The Steinheil spectrograph with three prisms was used; we applied both the high and the low dispersion.

The thoroughly purified nitrobenzol, obtained from the Institute of Reagents (Moscow), was of a slightly yellow-green shade. The latter did not change even after it had been illuminated for several hours with a quartz mercury vapor lamp. A series of spectrograms was obtained with a molecular concentration of nitrobenzol from 100 percent to 5 percent. By changing the time of exposure of solutions of various concentration we succeed in equalizing the intensity of certain lines which served for comparison. In this particular case it was the line corresponding to $\Delta\nu = 1341$ cm^{-1} (oscillations of the group NO_2). No marked changes of relative intensity of separate lines could be observed. This may be explained either by the fact that in nitrobenzol the association does not form clearly defined complexes or by the low frequency of vibration of the forming complexes and the impossibility under the conditions of our experiment of separating the corresponding lines from the exciting line. It must be pointed out, however, that nitrobenzol has an absorbing power that drops suddenly in the part of the spectrum lying between $\lambda = 436 m\mu$ and $\lambda = 491 m\mu$, and the majority of the lines compared were in that region. The different absorption might obscure the sought for effect of relative variation of intensity of separate lines. Of much greater interest are the results obtained for acetic acid. In this case we succeeded in discovering a definite frequency which seemed to correspond to the oscillations of one part of the complex relative to the other. Glacial acetic acid, also obtained from Institute of Reagents was studied at molecular concentrations of 100, 60, 40 and 20 percent. The spectrograms obtained lead to the conclusion that the lines corresponding to $\Delta\nu = 623$ cm^{-1}, represented on our spectrograms as satellites of $\lambda = 436 m\mu$ ($\Delta\nu = 22{,}938 - 22{,}315 = 623$ cm^{-1}) and of the line $\lambda = 405 m\mu$ ($\Delta\nu = 24{,}705 - 24{,}081 = 624$ cm^{-1}), changed their intensity markedly as compared with the other lines used for comparison. For the latter the lines were taken which corresponded to the frequencies $\Delta\nu = 855$ and $\Delta\nu = 2938$. While they are well defined and intense in pure acetic acid the lines corresponding to the frequencies $= 623$ cm^{-1} weaken considerably at 40 percent concentration and the satellite of $\lambda = 405 m\mu$ disappears completely at a 20 percent concentration, the satellite of the heavier line $\lambda = 436 m\mu$ being hardly visible.

The results obtained by us for acetic acid are in agreement with the Bhagavantam's[5] remark to the effect that the low frequencies in a combination spectrum of acetic acid disappear at high temperatures.

This gives us reason to believe that in acetic acid there takes place a formation of complex molecules of a quite definite configuration characterized by a definite energy of connection and a definite characteristic wave number $\Delta\nu = 623$ cm^{-1}.

Indirectly, the associative nature of this wave number is confirmed by the fact, that, according to Coblentz's[6] data, it is absent in the infrared spectrum of acetic acid; the associative frequency is not active and therefore must not appear in the absorption spectrum.

The results obtained for the associative frequency of complex molecules in connection with other data enable us to compute certain parameters, characterizing these molecules the nature of interacting powers, the distance between single molecules within a complex one, etc. The computation made for acetic acid gives quite admissible values.

The writers wish to acknowledge their indebtedness to Professor G. S. Landsberg, under whose direction the work was carried out.

[5] Bhagavantam, Ind. J. Phys. **5**, 48 (1930).
[6] Cited: Ganesan, Ind. J. Phys. **4**, 216 (1929).

Formation of Negative Ions in Gases by Electron Attachment

Part I. NH_3, CO, NO, HCl and Cl_2

NORRIS E. BRADBURY,* *Massachusetts Institute of Technology*

(Received October 4, 1934)

With the same method and apparatus employed in the study of negative ion formation in O_2 by electron attachment, the results have been extended to all the common diatomic gases and NH_3. No negative ions are formed in NH_3 below an X/p of 7.5; beyond that point they are formed with increasing probability as the energy of the electrons increases. The phenomenon is interpreted as dissociation of the molecule with the formation of NH^- at an electronic energy of approximately 3 volts, the NH_3 molecule having itself no electron affinity. No negative ions could be formed in CO at the electronic energies available, and the molecule is presumed to have no electron affinity. Negative ions are formed by electron attachment in NO, the probability increasing with decrease in electronic energy. A linear variation in probability of attachment with pressure is also observed in NO which is due to a collision with a pair of NO molecules held together by weak attractive forces. Negative ions are formed in HCl with a probability which increases with increasing electronic energy suggesting that dissociation of the molecule occurs here as well. Similar results are obtained in Cl_2 where it has been known that the energy of the attachment process must be more than sufficient to dissociate the molecule. The experiments indicate several types of attachment processes which can occur in gases and the possibilities of energy dissipation in ion formation. In general the most favored process is the carrying off of the energy by a third body involved in the process.

IT is well known that stable negative ions may be formed in many gases. Their formation is apparently the random capture of electrons by otherwise neutral molecules, though this phenomenon is by no means well understood. Its study in oxygen[1] has shown, however, that the attachment process and its variation with electronic energy furnish a most powerful tool for the study of the behavior of electrons in gases. Not only may the intrinsically interesting factors in negative ion formation be investigated, but the variations in the rate at which attachment occurs may be related to otherwise unobservable interactions between electrons and gas molecules. In addition the variation of the probability of the capture process with electron energy throws light on the most pressing problem of negative ion formation; namely, the disposition of the energy of binding, or the electron affinity, of the molecule. In consequence of these facts it has been of interest and importance to extend the experiments on oxygen to studies of the other common diatomic and polyatomic molecules. Part I of these papers deals with the ordinary diatomic molecules and also NH_3, and Part II with the triatomic molecules. They cover all the common gases of these types which are available for laboratory experimentation.

EXPERIMENTAL METHOD

The experimental apparatus was the same as that employed for the study of negative ion formation in oxygen and a detailed account has already been presented.[1] A brief description, only, will be given here. The principle of the method lies in the analysis of a mixed current stream of ions and electrons which is passed through a grid of fine wires. A high frequency alternating potential of the order of 50 volts and 10^6 cycles is applied between alternate adjacent wires of this grid. Under these conditions the electronic component of the current is swept out of the current stream to the grid wires, and the heavier and more slowly moving negative ions pass through essentially undisturbed. The difference between the current to the collector with no potential between the grid wires and that with a potential will be a measure of the ionic fraction of the current. A single grid of this type was used by Cravath[2] to measure the fraction of electrons remaining unattached at a given distance from a source of electrons. However, in practice some negative ions will be captured by the grid, and some electrons will escape. To avoid the resulting errors, *two* grids were employed in the present experiments, either one of which might be removed from the current stream while

* National Research Fellow.

[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).

[2] A. M. Cravath, Phys. Rev. **33**, 605 (1929).

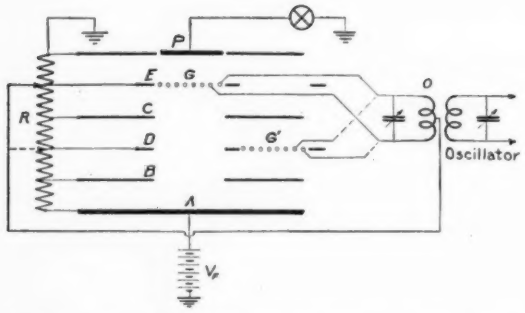


FIG. 1. Schematic diagram of apparatus. Alternate wires in grids G and G' are connected together and either grid may be moved into or out of the uniform field space.

the other was being used. Thus it was possible to study the decrease in the number of free electrons by attachment as they were drawn through the gas space between the grids. Any spurious effects due to the grids themselves effectively cancelled out.

A zinc plate parallel to the grids served as a photoelectric source of electrons, and a uniform field was maintained between it and the plane collecting electrode. A schematic diagram of the apparatus is shown in Fig. 1. By removing both grids from the current stream it was possible to obtain an estimate of the electronic mobility using the approximate equation given by J. J. Thomson.[3] This was necessary to evaluate the number of electronic impacts in going a given distance, and hence the probability of capture at a collision, denoted here by h.

The whole apparatus was contained within a large Pyrex tube which could be baked out and pumped down to 10^{-6} mm Hg before the admission of a sample of gas. A plane quartz window to admit ultraviolet light from a quartz mercury arc was affixed to the tube by means of a graded seal. Suitable filters were employed to cut out radiation harder than 2537A. A liquid air or solid CO_2 trap to condense Hg vapor was placed between the tube and all manometers, gauges, and pumps. To avoid contamination by stopcock greases, mercury cutoffs were substituted for all stopcocks. These could be adjusted to operate suitably under pressures of a few centimeters of Hg and proved very satisfactory. A specially designed McLeod gauge was employed to read pressures of the order of a few millimeters; otherwise a mercury manometer was used.

It has previously been shown in all work of this type that great care must be taken to maintain extreme gas purity; consequently each gas was purified according to its particular requirements. Several separately purified samples of gas were used in each case, and agreement of the results from the various samples was taken as an indication of purity. Only in rare instances was difficulty experienced in adequately purifying the gas to be studied. These particular cases will be noted later.

AMMONIA

The formation of negative ions in ammonia has been the subject of investigation and discussion. Bailey and Duncanson[4] observed the presence of negative ions in ammonia gas at values of X/p greater than 10 (X in volts/cm and p in mm Hg). On the other hand, using very pure samples of ammonia Loeb[5] was unable to obtain any trace of negative ions under the conditions of his experiment. The causes and conditions of so marked a discrepancy therefore are of considerable interest.

The ammonia used in the following experiments was obtained from a commercial tank of anhydrous NH_3 of which approximately one-half had already been used. Most of the residual hydrogen had, therefore, been blown off. The gas was liquefied over metallic sodium and dried for several days. It was then solidified with liquid air and any uncondensable gas pumped off. This process was repeated and the final sample fractionally distilled, only the middle portion being retained for the experiments.

The results of the measurements at different pressures and values of X/p are given in Fig. 2 in which h, the probability of attachment, is plotted as a function of X/p. The curve shows that for low electron energies (of which X/p is a measure) the ammonia molecule *does not form*

[3] J. J. Thomson, *Conduction of Electricity through Gases*, p. 466, University Press, Cambridge, 1928.

[4] V. A. Bailey and W. E. Duncanson, Phil. Mag. **10**, 145 (1930).

[5] L. B. Loeb, Phil. Mag. **8**, 98 (1929); H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

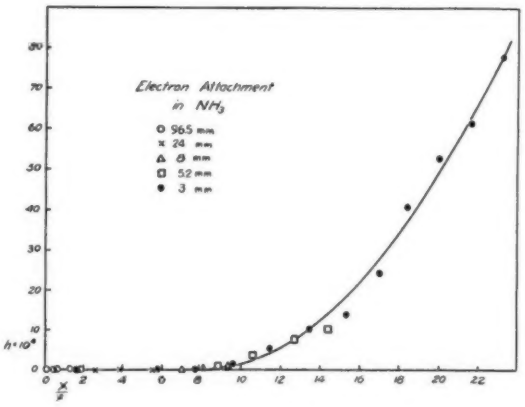


FIG. 2. Probability of electron attachment in NH_3. The points indicate data taken at different pressures as shown.

negative ions. This is in accord with the observations of Loeb. At a value of X/p about 9, however, negative ions begin to appear in the gas and are formed in increasing numbers as the field strength is increased. Thus the observations of both Loeb and Bailey are entirely compatible, their observations merely differing in range of electronic energy studied. Loeb did not investigate values of X/p greater than 0.1.

It is not apparent, however, why an ammonia molecule should possess an electron affinity for high energy electrons and not for those of low energy. The interpretation must be that some change is induced in the ammonia molecule by electrons of energy greater than a certain amount, and that attachment takes place as the result of this change. The most probable process which can occur is some type of dissociation. This possibility of dissociation occurring in certain attachment processes was suggested by James Franck as early as 1928 on the basis of Loeb's observations of various apparent classes of attaching molecules.

The photochemical decomposition of ammonia has been extensively studied and the most probable reactions set forth. Two possible initial steps may be proposed. They are, with the corresponding energies,

$$NH_3 + h\nu \rightarrow NH_2 + H, \quad E \geqq 4.7 \text{ volts}, \quad (1)$$

$$NH_3 \rightarrow NH + H_2, \quad E = 3.0 \text{ volts}. \quad (2)$$

Wiig and Kistiakowsky[6] have shown that (1) occurs in the photochemical decomposition of NH_3 followed by subsequent secondary reactions which lead eventually to the formation of N_2 and H_2. Koenig and Wagner,[7] however, have found that by decreasing the electric current in silent ammonia discharges a reaction to hydrazine may be made to occur almost quantitatively. Such a reaction as the result of electron impact is better explained by (2) above rather than as a secondary reaction of (1). Gedye and Allibone[8] have also observed the formation of N_2H_4 in the decomposition of NH_3 by high speed electrons.

It seemed very probable that some reaction of this type occurred in the process of electron attachment at high X/p. No resultant H_2 could be detected, however, after freezing out all the ammonia with liquid air at the conclusion of an experiment. This was to be expected, however, from the volume of the tube and the magnitude of the electronic currents employed. Accordingly a very much smaller tube was constructed with small plane polished zinc electrodes. Electron currents of the same or greater intensity could be obtained from this tube, and the smaller volume multiplied any residual hydrogen pressure by a factor of 10. Using ammonia pressures of the order of 5 mm, the curve shown in Fig. 3 was obtained, the pressures being read on a McLeod gauge after freezing out the NH_3 with liquid air. To eliminate photodecomposition of the ammonia a 20 cm filter of NH_3 gas at two atmospheres pressure was employed. The experiments were difficult because of the extremely minute quantities of gas involved, but showed definitely that at even moderately low fields a residual gas, uncondensable by liquid air, is produced by the passage of electrons through ammonia. Furthermore, the appearance of this gas occurs at approximately the same value of X/p as that at which negative ions begin to be formed.

It is therefore suggested that the NH_3 molecule *does not* form a stable negative ion, but that

[6] E. O. Wiig and G. B. Kistiakowsky, J. A. C. S. **54**, 1806 (1932).
[7] Koenig and Wagner, Zeits. f. physik. Chemie **A144**, 213 (1930).
[8] Gedye and Allibone, Proc. Roy. Soc. **A130**, 346 (1931).

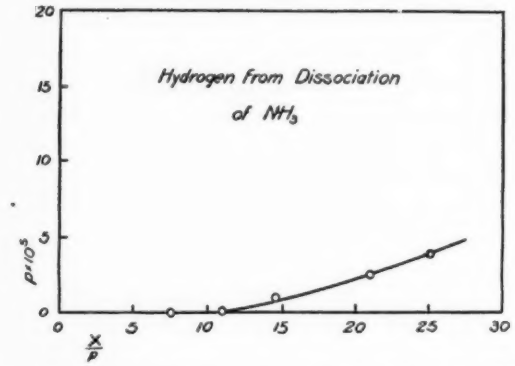


FIG. 3. Residual gas, uncondensable by liquid air, formed by the passage of electrons through NH_3.

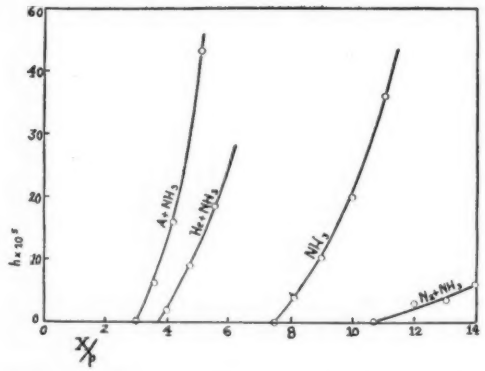


FIG. 4. Probability of attachment in mixtures of NH_3 with the inert gases showing variation in rate of gain or electron energy.

negative ions in ammonia are formed, probably in a single elementary process, by the reaction

$$NH_3+e\rightarrow NH^-+H_2.$$

The ion which finally results may be of the order of $N_2H_4^-$ by a secondary process. There are two reasons for suggesting that the decomposition and attachment occur in a single process. In the first place such a reaction affords a most convenient means for dissipating the energy of attachment, as it is not necessary to call upon either radiation or a three body collision to account for its disappearance. This question will be discussed in more detail at another point. Secondly, if dissociation occurs followed by subsequent attachment of *another* electron, then the probability of such an attachment would have to be nearly unity as the actual concentration of the products is so minute.

It, therefore, seems probable that the process of negative ion formation in NH_3 is not one of attachment to the ammonia molecule, but a simultaneous process of dissociation and attachment to one of the products formed. It is probable that the electron energy required for this process to occur must be close to that required for dissociation, as the electron affinity is small and cannot be available until dissociation can nearly be brought about by the electron itself. The rise in the curve then occurs as the energy of the electrons increases and dissociation becomes more probable.

Further evidence of the fact that inelastic impacts occur in ammonia at values of X/p of the order of magnitude of 10 is shown by the mobility curve of electrons in ammonia which was found to increase at that point. On the Compton[9] theory of electronic mobilities this behavior is an immediate consequence of such impacts.

As a further test of this theory of negative ion formation, experiments were carried out with mixtures of NH_3 and the inert gases N_2, A and He. In the experiments on oxygen, such mixtures were shown to affect the rate at which electrons gained energy in the gas without changing the character of the attachment curve, its position on an X/p scale only being shifted. The results of such measurements in NH_3 are shown in Fig. 4. From these curves and data of Townsend[10] on electron energy in gases as a function of X/p, it is possible to estimate the energy at which the formation of negative ions begins to occur. This gives a value of about 4 volts and is of the correct order of magnitude for the process suggested. Definite proof that this is the correct explanation of the phenomenon must await mass-spectrographic analysis of the products. It seems, however, strongly suggested by the present observations.

CARBON MONOXIDE

Carbon monoxide was prepared from pure sodium formate and concentrated sulfuric acid, all air and water vapor being removed by evacu-

[9] K. T. Compton, Rev. Mod. Phys. **2**, 231 (1930).
[10] J. S. Townsend, Jr., J. Frank. Inst. **200**, 563 (1925).

ating the reaction flask before adding the sulfuric acid. The CO so formed was passed over hot copper shot and through several liquid air traps for complete drying.

No attachment was observed in CO at any value of X/p between 0.25 and 20, the practical limits of the apparatus. The observational limit of the apparatus is a function of pressure, but one may determine probabilities of capture greater than 10^{-8} at the higher pressures and 10^{-7} at lower pressures (5 mm). Any attachment in CO is therefore less than these probabilities and is presumably zero.

Electron attachment in CO has been studied by Wahlin[11] who found a coefficient of the order of 10^{-8} but suggests that the value might be zero. This agrees with the present measurements and it is therefore concluded that *CO has no electron affinity* and under ordinary conditions, negative ions cannot be formed in it. Since the energy required to dissociate CO is about 9.0 volts, it is probable that electrons within this range of X/p do not attain this energy. Negative O^- ions have been observed in CO at low pressure by Tate and Lozier[12] when the energy of the bombarding electron exceeded 10 volts. Such a process could doubtless be made to occur at ordinary pressures provided the electron energy reached the proper amount. The measurements of Townsend,[10] however, indicate that even at an X/p of 20, the energy is hardly 2 volts. The similarity of the electronic structure of CO to that of N_2 makes quite reasonable its lack of an electron affinity.

Nitric Oxide

Nitric oxide was prepared by two different methods since the character of the results obtained showed that definite and unambiguous purity was necessary. The gas was first prepared by the decomposition of a dilute sodium nitrite solution in an air free flask with sulphuric acid. The gas so formed was passed over P_2O_5 and solidified in a trap cooled with liquid air. The other means of preparation, which was simpler and equally satisfactory, was by the thermal

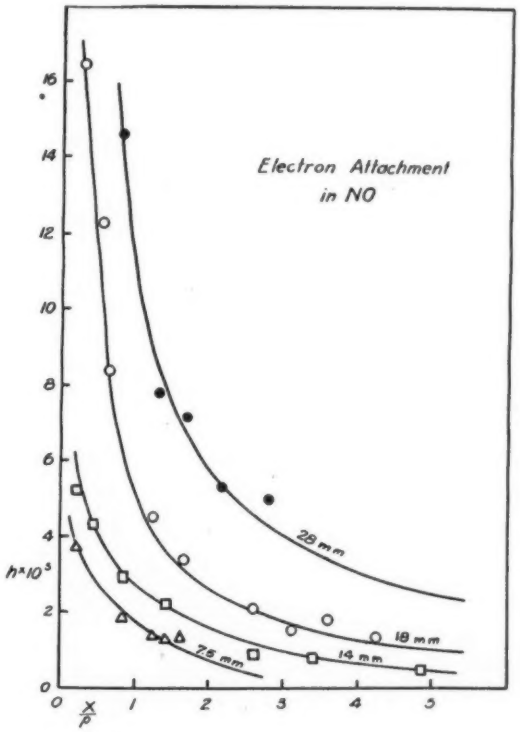


FIG. 5. Probability of electron attachment in NO. The different curves are for different pressures as shown.

decomposition of diphenyl nitrosoamine. Eastman's practical grade was employed and heated below the temperature of decomposition (140°) for some time in a vacuum. The temperature was then raised to 140° and the gas collected in a liquid air cooled trap. As far as could be determined, the resulting NO was extremely pure. The gas was fractionated from the solid state and passed through traps held at −150° into the measuring chamber. The use of mercury cutoffs in place of ordinary stopcocks was particularly advantageous with this gas. The presence of any O_2 would have been indicated by a red color from NO_2 formed, and the latter gas would have been frozen out in the protecting traps.

The results obtained in this gas are shown in Fig. 5 where the probability of attachment is plotted as a function of X/p. Almost alone of all gases studied, there was here observed a definite *variation of the probability of attachment with pressure.* The curves indicate a marked increase in attachment with increase in pressure. To make doubly certain that the effect was not due to

[11] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).
[12] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

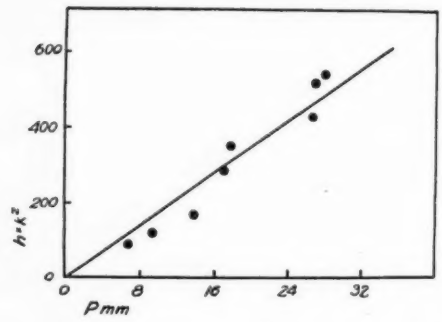


FIG. 6. Variation in the probability of electron attachment in NO with pressures. The electron energy corresponds to that for $X/p=1.5$.

impurities, experiments were made on a single sample of gas which was pumped down from the higher pressures to the lower, the runs in each case being taken at the same X/p. The points so obtained were used as the basis for Fig. 6 and the data from the curves in Fig. 5 plotted there as well. It is seen that the attachment coefficient at a given X/p is a linear function of the pressure. Such a variation immediately suggests that some form of triple collision occurs since an increase in pressure increases the fraction of all collisions which are of the three body type.

Inasmuch as a three body process has often been put forward as one of the means of dissipating the energy of attachment, if was of interest to investigate the effect further in this gas. A mixture of equal parts of N_2 and NO was made up and attachment investigated in this artificial gas. N_2 was chosen as it is the most nearly similar in mass to NO of the inert gases. In such a mixture, three kinds of triple collisions may take place. They are:

$$N_2+ N_2+e$$
$$N_2+NO+e$$
$$NO+NO+e$$

The first of these will not result in a negative ion. *A priori*, either of the other two processes might be equally effective, and hence, if results were compared at the same pressure, the value of h for the mixture should be 2/3 that for NO. Actually, however, it is about 1/3 showing definitely that *two molecules* are involved in the attachment process and *that they are both NO molecules.*

It is, therefore, suggested that in the case of NO, we are dealing, in the primary attachment process, not with NO, but with a labile, lightly bound polymer of NO, i.e., $(NO)_2$. NO is one of the well-known "odd" molecules, and, in view of the tendency of such molecules to polymerize, it has been a most interesting exception. There is, however, evidence for its association into double molecules at low temperatures, and Kassel[13] has calculated the energy of attraction between two NO molecules. This comes out to be as much as 0.05 volts. The electronic structure of NO has been discussed by Pauling,[14] and reasons have been presented why NO may not polymerize to any great extent. However, in consequence of these experiments, the character of the molecule, and its known association at low temperatures, it is suggested that lightly bound polymers of NO do occasionally occur. Negative ion formation in NO is then to be explained by the formation of NO^- from one of these temporarily existing pairs, the other molecule of NO carrying away the excess energy of the reaction. Triple collisions of the kinetic theory type when no intermolecular forces exists are probably too rare to account for negative ion formation, but the existence of slight intermolecular forces is sufficient to enormously increase their frequency. While the deviation of NO from a perfect gas is not excessively great, it is of sufficient magnitude to permit this explanation.

The rate of negative ion formation in NO has not previously been studied and there are no data with which to compare these results. Negative ions with high velocity electrons (~10 volts) have been observed in NO by Tate and Smith[15] and also Hogness and Lunn,[16] but the ions formed are largely atomic and due to processes involving dissociation.

CHLORINE AND HYDROGEN CHLORIDE

The great rapidity with which these molecules apparently attach free electrons as well as their great chemical reactivity made measurements in

[13] L. S. Kassel, *Kinetic of Homogeneous Gas Reactions*, p. 170, Chemical Catalog Co., New York, 1932.
[14] L. Pauling, J. A. C. S. **53**, 3225 (1931).
[15] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).
[16] Hogness and Lunn, Phys. Rev. **30**, 26 (1927).

these gases extremely difficult. Attachment was so rapid that at even the lowest pressures at which the grids would function (~2 mm) no measurements were possible. The device of dilution with an inert gas, usually argon, was therefore resorted to since the mixture experiments had always showed that the character of the curves was unchanged under such circumstances. Under these conditions the grids functioned properly, yet the concentration of the active gas was small enough to permit measurements to be made.

Hydrochloric acid gas was prepared by dropping concentrated sulfuric acid on NaCl in a vacuum. The resulting product was frozen, any uncondensable gas pumped off, and the final product fractionally distilled. The gas was passed through traps held at −115° before admission to the measuring chamber. Under these circumstances a gas of such purity and dryness was obtained that ample photoelectric currents could still be obtained from the zinc photoelectric surface. The diluting gases were purified in the usual manner with hot copper shot and liquid air cooled traps.

The results are shown in Fig. 7. In this case the values of X/p are those for the gaseous mixture of argon and HCl and must not be considered as applying to the undiluted gas. It is seen that attachment occurs in HCl for electrons even of very low energy, and that the probability of attachment increases rapidly as the energy of the electrons is increased. This latter phenomenon seems to indicate that negative ions are formed in HCl as the result of a dissociation process similar to that observed in NH_3. The reaction probably occurring would be of the form

$$HCl+e\rightarrow H+Cl^-.$$

The energy of dissociation of HCl is 4.5 volts and the electron affinity of the Cl atom, calculated by means of the Born cycle,[17] is about 4.1 volts. Thus energy is available for the dissociation process at even low electron energies, and the presence of negative ions in the gas, indicated by mobility experiments, at low values of X/p can be explained on this basis. As the energy of the electrons is increased, dissociation and the formation of Cl^- becomes more probable and the rate of negative ion formation increases. Such a process permits a kinetic disposition of the energy of binding, and seems to be in accord with the experimental observations. Further support for such an interpretation is found in the work of Barton[18] who found only Cl^- ions in HCl with even very slow electrons. It is therefore suggested that the negative ion initially formed in HCl is not HCl^- but Cl^-. These experiments are also in accord with those of Bailey[19] who observed attachment in HCl at high values of X/p. He found that the probability of attachment increased as X/p increased, the most rapid rise occurring at an X/p of 15. This is undoubtedly the same phenomenon as observed here.

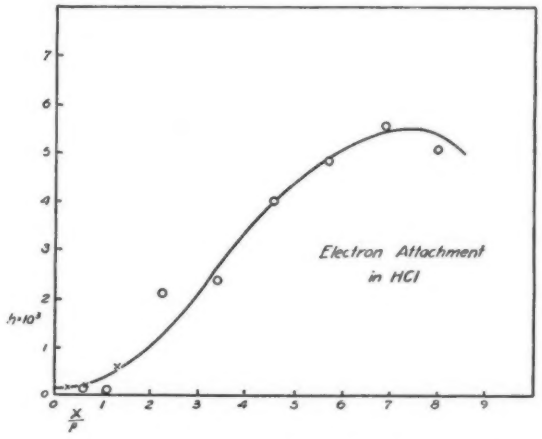


FIG. 7. Probability of electron attachment in HCl (in argon mixtures).

The experiments with chlorine presented even greater difficulty than those with HCl. The gas was prepared by the thermal decomposition of $CuCl_2$ in the manner described by Loeb[20] with great care to keep the system thoroughly dry. In spite of this, a considerable decrease in the photoelectric activity of the plate was observed. However, measurable currents could still be obtained, and the results of experiment with argon dilution are shown in Fig. 8. Here it is to be expected that a process of dissociation would occur since the dissociation energy of the Cl_2 molecule is only of the order of 1.5 volts. There

[17] J. Sherman, Chem. Rev. **11**, 93 (1932).

[18] F. A. Barton, Phys. Rev. **30**, 614 (1927).
[19] V. A. Bailey and W. E. Duncanson, reference 4.
[20] L. B. Loeb, Phys. Rev. **35**, 184 (1930).

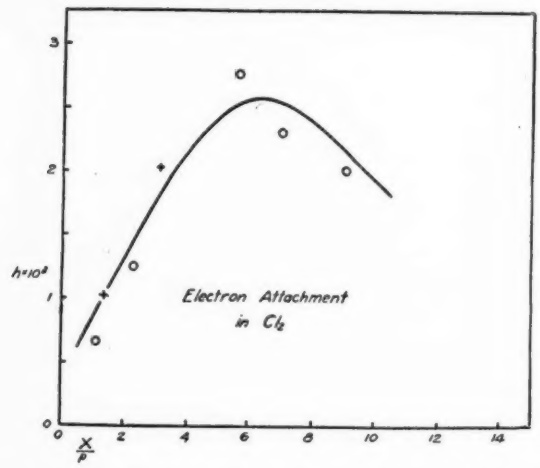


FIG. 8. Probability of electron attachment in Cl_2 (in argon mixtures).

is thus available ample energy to dissociate the molecule with the formation of Cl^-, and the character of the curve, rising with increase in electronic energy substantiates this interpretation. This is also in accord with the observations of Hogness and Harkness[21] on the formation of negative ions in I_2 at very low pressures. They observed as a primary process only the formation of I^- even at very low electron energies. A similar behavior would be expected in Cl_2. The only quantitative measures of the probability of attachment in Cl_2 are those of Wahlin[11] who found an approximate value of 10^{-3} in good accord with the present measurements.

DISCUSSION

As has been indicated, one of the greatest problems of negative ion formation is the means of dissipation of the energy of binding. Three *a priori* possibilities are available for this. They are: (1) radiation; (2) three body collision; (3) dissociation and simultaneous attachment. Of these three processes, (2) and (3) are not essentially dissimilar since both involve the removal of the energy as kinetic energy by a third body. Various attempts have been made to observe the radiation emitted in the formation of negative ions, but the experiments have been complicated by a lack of intensity or other factors. Oldenburg[22] attempted to observe an electron affinity spectrum from the iodine atom but without success. However, in certain cases, notably O_2 and SO_2, there seems to be fairly definite evidence that an O_2^- or an SO_2^- ion is formed. In such a case there is no process except radiation which can carry off the excess energy. Since the probability of attachment *increases* for very *slow* electrons, the energy of the electron cannot play any part in a dissociation process, and the energy of attachment cannot be as much as the 5.4 volts necessary for dissociation. Other considerations as well seem to point to the existence of an O_2^- ion. Erikson[23] has found that the mobilities of newly formed positive and negative ions were the same, and Luhr[24] has shown that even in a glow discharge, 95 percent of the positive ions formed are O_2^+. The aging experiments thus point to an initial equality of mass and hence to an O_2^- ion. The question cannot be settled definitely, however, without mass-spectrographic analysis.

Of the three types of attachment process, all apparently can and do occur. That of dissociation and attachment in a single elementary process, in which the energy is carried off by the particles themselves, is apparently the most common and readily occurring. It occurs in NO though here the electron affinity is sufficient to break the apparently weak binding forces, and the kinetic energy of the electron plays no part other than to decrease the probability of attachment as its energy increases. Further examples of the more common type of curve, where the probability of attachment increases with increasing electronic energy, and which is interpreted as a dissociation process, will be discussed in Part II.

[21] Hogness and Harkness, Phys. Rev. **32**, 784 (1928).

[22] O. Oldenburg, Phys. Rev. **43**, 543 (1933).
[23] H. A. Erikson, Phys. Rev. **30**, 339 (1927).
[24] O. Luhr, Phys. Rev. **44**, 459 (1933).

The Formation of Negative Ions in Gases

Part II. CO_2, N_2O, SO_2, H_2S and H_2O

NORRIS E. BRADBURY* AND HOWARD E. TATEL, *Massachusetts Institute of Technology*

(Received October 4, 1934)

The study of electron attachment has been extended to the gases CO_2, N_2O, SO_2, H_2S and H_2O. No negative ions were observed in CO_2. In N_2O, below $X/p=2$, no negative ions were formed, and the N_2O molecule apparently has no electron affinity. For values of $X/p>2$, the electrons possessed sufficient energy to dissociate the molecule and negative ions, probably O^-, were formed in increasing numbers. SO_2 showed an electron affinity forming negative ions with electrons of very low velocity. The probability of attachment decreased as X/p increased until an X/p of about 13 when an increase in probability of formation was noted. This is probably due to dissociation and formation of SO^-. No negative ions were observed in H_2S below an X/p of 6. For greater values of X/p negative ions were formed in increasing amounts presumably by a dissociation process with the formation of HS^-. A similar behavior was observed in H_2O at an $X/p=10$, with the formation of OH^-. Negative ion formation in H_2O was also observed at low X/p and varied with the pressure of the gas. This is explained as being due to negative ion formation from small molecular aggregates existing near the point of condensation of the water.

THE formation of negative ions by electron attachment in the common diatomic gases has been reported in the preceding paper. It was possible, there, to interpret the characteristics of the observed attachment processes in terms of known molecular constants and properties. Extensive experimental work in both electron bombardment and band spectroscopy of such molecules has made available a great amount of pertinent data, thereby greatly simplifying the analysis of the energy relations in negative ion fromation. The study of electron attachment in ammonia, however, showed that it was possible to interpret the phenomena occurring fairly satisfactorily, even where detailed knowledge of the electronic properties of the molecule was lacking. It was, therefore, of great interest to extend the data to include the common triatomic inorganic molecules. The results given here were taken with the same apparatus and methods described in Part I.

NITROUS OXIDE

Nitrous oxide was obtained from a commercial tank of the gas of high purity. The gas was solidified in a trap cooled with liquid air, and any uncondensable gases pumped off. This process was repeated and the resulting product twice fractionated with liquid air. The middle third of the final sample was retained for use. In all these experiments, it was generally found that physical methods of purification were not only simpler than chemical means, but lead to a purer product.

The results of the experiments are shown in Fig. 1 where the probability of electron attachment at a single collision, h, is plotted as a function of X/p, the field strength in volts/cm divided by the pressure in millimeters of Hg. It is seen that no attachment occurs for small values of X/p, and that therefore, the N_2O molecule *has no electron affinity*. However, at an X/p greater than 2, negative ions are formed in the gas and continue to be formed in increasing numbers as the value of X/p is increased. This is a type of process which has been observed in NH_3 (Part I) and it has been shown that dissociation is apparently typified by such an attachment curve. The most interesting feature of this case is the low energy at which the process seems to occur.

Electron attachment has been studied in N_2O by Bailey and Rudd,[1] and though they do not carry their curve to a very low value of X/p, the general behavior is the same as that reported here, a probability of attachment increasing with increasing X/p. They also find that at very high X/p of the order of 25 the probability of attachment decreases somewhat. This observation was beyond the range of the present apparatus.

* National Research Fellow.

[1] Bailey and Rudd, Phil. Mag. **14**, 1033 (1932).

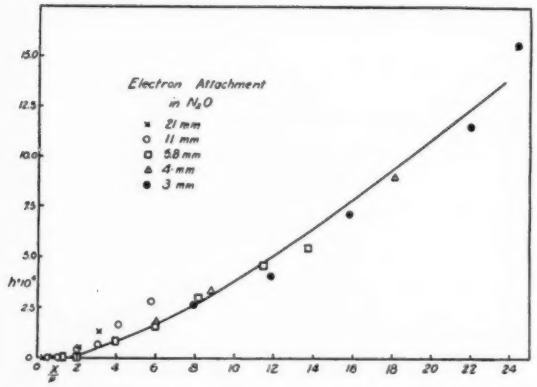


FIG. 1. Probability of electron attachment in N_2O. Data taken at different pressures as shown.

The decomposition of N_2O, by both thermal and photochemical means, has been extensively studied, though the results are not highly concordant. Two processes are possible for the decomposition:

$$N_2O \rightarrow NO + N, \quad (1)$$

$$N_2O \rightarrow N_2 + O. \quad (2)$$

The energy required for reaction (1) is 4.7 volts and that for reaction (2) is 1.8 volts. The first reaction has been shown to occur for the photochemical process by Dutta[2] who observed continuous absorption to set in at 2750A and this interpretation is further supported by observations of Wulf and Melvin[3] who found NO bands appearing in irradiated N_2O. On the other hand, the thermal reaction has been definitely shown[4] to follow (2) with a slightly higher energy of activation.

To determine which of the reactions occurred in the present case, the expedient of mixing N_2O with inert gases was tried. The results are shown in Fig. 2. It is seen that for low energies at least, electrons gain energy in N_2 at much the same rate as in N_2O. It is then possible to determine from data of Townsend[5] on electron energies in N_2, the approximate energy at which attachment begins to occur. This is approximately 1.7 volts for the foot of the curve, a value which is

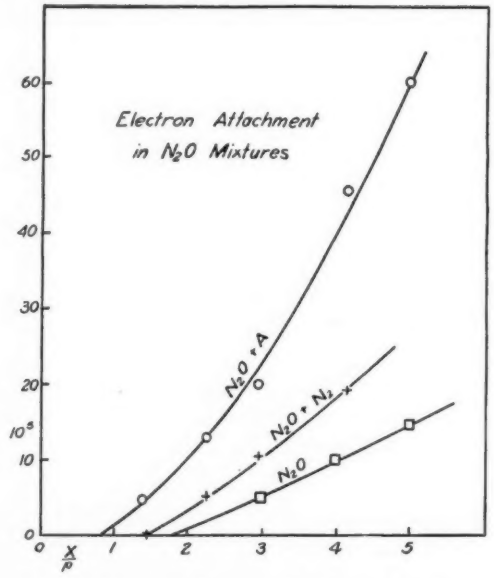


FIG. 2. Probability of electron attachment in mixtures of N_2O with equal parts of the inert gases, N_2 and A.

in excellent agreement with the value for reaction (2) above.

Hence the most probable mechanism for negative ion formation in N_2O is a reaction of the type

$$N_2O + \epsilon \rightarrow N_2 + O^-.$$

Since N_2 does not form negative ions, at least in the unexcited state, it is probable that the initial ion formed is O^-. The subsequent character of the ion can be determined only by other methods. This is, apparently, another example of simultaneous attachment and dissociation and the products of the reaction are available to carry off the excess energy. It may be noted in both this experiment and in that with NH_3 that the electronic reaction is not necessarily the same as the photochemical reaction. Where two types of dissociation are possible, that of the lower energy may first occur with electron bombardment when it does not appear photochemically.

CARBON DIOXIDE

Carbon dioxide was obtained from a commercial tank of anhydrous CO_2 and purified in a manner similar to N_2O. Solid CO_2 snow was kept on all traps during the course of the experiment to condense Hg vapor.

[2] A. K. Dutta, Proc. Roy. Soc. **A138**, 84 (1932).
[3] Wulf and Melvin, Phys. Rev. **39**, 180 (1932).
[4] L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 227, Chem. Catalog Co., New York (1932).
[5] J. S. Townsend, J. Frank. Inst. **200**, 563 (1925).

No attachment was observed in CO_2 even at the highest X/p which could be studied. Since the lowest energy required for the dissociation of CO_2 into CO+O is 5.5 volts, it seems probable that electrons, at moderate values of X/p, do not easily attain this energy. This conclusion is supported by Townsend's data for CO_2. Negative ion formation has been studied in CO_2 by Loeb[6] and Wahlin.[7] Loeb found values as low as 10^{-7}, but the value varied with the age of the gas indicating the presence of contamination from the walls of the chamber. It therefore seems reasonable to assert that the probability of attachment in CO_2 must be less than 10^{-8} and that apparently CO_2 *does not form negative ions.*

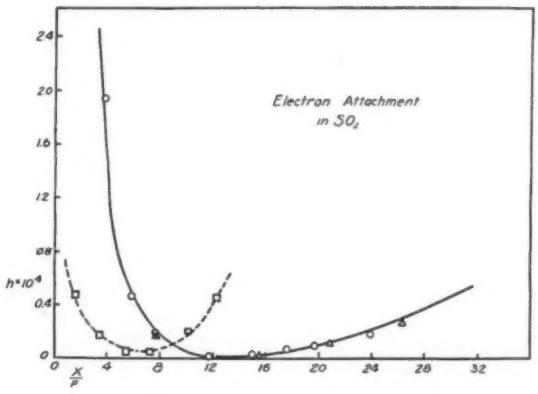


FIG. 3. Probability of electron attachment in SO_2. The dotted curve is the probability of attachment in a mixture of equal parts of SO_2 and argon.

SULFUR DIOXIDE

Sulfur dioxide was obtained from a commercial tank of the anhydrous gas. It was first passed through a long tube of P_2O_5 and then condensed at low pressure in a trap cooled with liquid air. Any residual gas was then pumped off and the process repeated after remelting the sample, which was then fractionated in the usual manner. CO_2 cooled traps were employed before the tube and for further drying, though they required that the experiments be made at pressures of SO_2 less than 4 mm.

The results for SO_2 are plotted in Fig. 3 where the probability of attachment is represented as a function of X/p. In SO_2, as in oxygen, attachment definitely occurs for electrons of low energy and increases rapidly as the energy of the electrons decreases. This indicates that the SO_2 molecule must have an electron affinity and that some radiative process occurs for the dissipation of energy. As the electronic energy increases, the probability of attachment at first decreases, and then begins to increase. A similar phenomenon was noted in O_2. This increase may be due either to a dissociation process or to an inelastic impact (as in O_2), reducing the electron energy to zero with consequent increased probability of capture.

To determine at approximately what energy the rise in the probability of attachment occurred, mixture experiments were made with argon and the X/p of the minimum points extrapolated to zero concentration of SO_2. This, using Townsend's tables, gives only a rough estimate of the electron energy, but determines, at least, an order of magnitude. The value so obtained is 4–6 volts for the electron energy at which the probability of attachment begins to increase.

There is very little spectroscopic, photochemical, or electronic data with which to compare this value. The energy of dissociation of SO_2, calculated from spectroscopic data, is given by Franck[8] for the two possible cases as:

$$SO_2 \rightarrow SO + O \quad 5.70 \text{ volts}, \qquad (1)$$

$$SO_2 \rightarrow S + O_2 \quad 5.71 \text{ volts}. \qquad (2)$$

Obviously, with energies so nearly equal it is impossible to determine which reaction, if either, occurs. Comparison of the observed and calculated energies seems to indicate, however, that dissociation is occurring, though from these data alone it is impossible to determine which of the four possible initial ions is formed. Reaction (1) seems the most probable in the light of all evidence and SO^- is suggested as the ion initially formed at values of $X/p > 14$.

HYDROGEN SULFIDE

Hydrogen sulfide was first obtained from a commercial tank of the gas and purification

[6] L. B. Loeb, Phys. Rev. **17**, 89 (1921).
[7] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

[8] Franck, Sponer and Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).

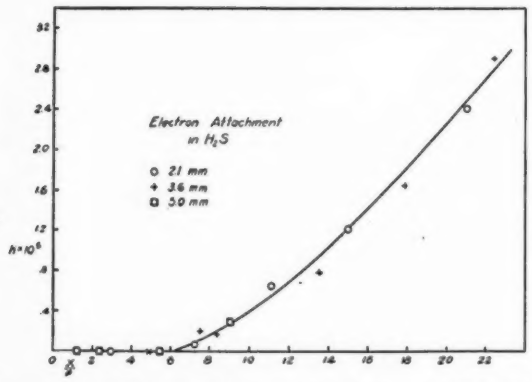


FIG. 4. Probability of electron attachment in H_2S. The data were taken at different pressures as indicated.

attempted in the usual manner. Experiment, however, showed that even after fractionation, the gas obtained was not entirely pure. The gas was therefore prepared by the cold hydrolysis of Al_2S_3 which gave a product of high purity.

The results of the experiment are shown in Fig. 4. It is seen that no attachment occurs for low values of X/p, and consequently the H_2S molecule has no electron affinity. However, at an X/p of 6, negative ions begin to be formed in the gas and are formed with increasing probability as the energy of the electrons increases. This again is most easily interpreted as a dissociation process of which two types are possible. They are:

$$H_2S \rightarrow H_2 + S \quad 3.2 \text{ volts}, \qquad (1)$$

$$H_2S \rightarrow HS + H \quad 3.7 \text{ volts}. \qquad (2)$$

The photochemical decomposition of H_2S has been studied by Stein,[9] but he was unable to interpret his results unambiguously. The present experiments cannot discriminate between two reactions which require so nearly equal amounts of energy. However, from analogy with water, in which the OH^- ion has been observed in electron bombardment experiments, it is probable that the same type of dissociation occurs here, and the initial ion formed is SH^- according to reaction (2) above. This energy is in accord with that determined from argon mixtures.

The formation of negative ions in H_2S has not been studied directly, but some experiments of Loeb[10] are interesting in this connection. In studying the mobility of negative ions in highly purified samples of H_2S, he observed that at certain values of the field strength he obtained only free electrons in the gas. For higher fields negative ions were again observed and also for lower fields. The effect was transient and greatly dependent on the purity of the gas. These results are easily explained by the present experiments.

The formation of negative ions at low fields was presumably due to slight traces of impurity which is not improbable in view of the difficulty of completely purifying this gas. (Similar effects were observed with the tank samples of gas in the present experiments.) At moderate values of X/p (~ 4) no ions were obtained, and at values greater than 6, negative ions were formed by the dissociation indicated above.

WATER VAPOR

Samples of distilled water were difficult to purify owing to the presence of dissolved gases which were hard to remove completely. It was found more satisfactory to prepare water vapor from carefully purified hydrogen and pure copper oxide which had been drastically heated in vacuum. The water thus prepared was frozen with liquid air and any excess hydrogen pumped off. Since hydrogen does not attach electrons, its presence in very small amounts would be harmless, while, as will be seen later, the oxygen or CO_2 dissolved in distilled water would have seriously affected the results.

The probability of the formation of negative ions by electron attachment in water vapor is plotted in Fig. 5. Owing to the similarity of their electronic and chemical properties, H_2O and H_2S would be expected to show similar behavior in forming negative ions. At low pressures this prediction is verified. For higher pressures, however, there is definite attachment and formation of negative ions even at low values of X/p. The explanation for this deviation from the character of the process observed in H_2S is simple, and is due to the fact that at the moderate pressures and room temperature water vapor is approaching condensation. Hence, there may exist large numbers of small aggregates and these should be very effective in forming negative ions. Otherwise, at lower pressures, where such groups will

[9] N. O. Stein, Trans. Far. Soc. **29**, 583 (1933).
[10] Loeb and Du Sault, Proc. Nat. Acad. Sci. **14**, 192 (1928).

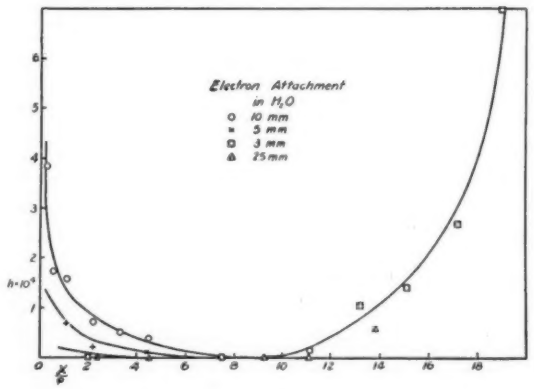


FIG. 5. Probability of electron attachment in H_2O. The various curves are for different pressures as shown.

be far fewer, the water molecule behaves as does the H_2S molecule and shows no electron affinity.

At higher values of X/p, there is distinct evidence of a dissociation process similar to that observed in H_2S. The energy required for the reaction

$$H_2O \rightarrow H + OH$$

is about 5.4 volts, a value which is reasonable in these experiments and which was substantiated by the usual argon mixtures. Hence, the probable elementary process occurring in the formation of negative ions in water vapor at high X/p is that given by the above process with the formation of OH^-. This ion has been observed by Smyth and Mueller[11] and others and certainly does exist. H^- has also been observed, but the conditions for its formation are so unique that it is doubtful if it occurs here.

Cravath[12] has briefly reported some interesting results on the effect of water vapor on the attachment process in oxygen. For water vapor alone he found a probability of attachment not greatly different in order of magnitude from that of oxygen. Under the circumstances of his experiment, he was undoubtedly studying the low X/p portion of the curves at the higher pressures given in Fig. 5. He also found that when water vapor and oxygen were mixed, more attachment was obtained than with either alone. Since mixture experiments with argon had given no indication of such an effect, other gases were tried. In order not to complicate the results, only gases which did not form negative ions were studied in the mixtures. Nitrogen was found to behave normally. CO_2, on the other hand, was found to produce many ions when mixed with water vapor. The explanation, then, of these results and those of Cravath must be that in the case of O_2 and CO_2 considerable intermolecular forces exist between these molecules and water molecules. Their solubility in water is an indication of this. It has been seen that whenever strong intermolecular forces exist, and polymers and compounds result (as apparently in NO and water) ready attachment to such compounds may occur. In general, it can be predicted that the effect of water vapor will be greatest in those gases which are highly soluble in water.

Bailey [13] has studied the formation of negative ions in H_2O and has found a probability of attachment which rises very rapidly from an X/p of 12. He did not investigate it at lower electron energies, but his observations are in agreement with the present experiments.

CONCLUSIONS

Of the triatomic molecules studied, SO_2 alone apparently has a real electron affinity. Mulliken[14] has suggested that both N_2O and CO_2 are linear molecules of similar electronic structure. It is therefore reasonable that if one of these molecules has no electron affinity, that the other should lack it as well. H_2S and H_2O behave in similar fashions, and would probably show identical behavior if H_2S were studied near its point of liquefaction. In all this work the fallacy of attempting to describe the electron affinity of a molecule from experiments in a single energy range has been very evident. As a result, a true electron affinity of a stable molecule is a much rarer quality than has been commonly supposed, though negative ions do exist in a large number of gases under certain conditions. A study of the mobility of some of these ions for very short ages might prove of considerable interest.

It is a pleasure to acknowledge indebtedness to the Massachusetts Institute of Technology for the facilities of their laboratories and to the staff of the department of physics for many helpful suggestions.

[11] Smyth and Mueller, Rev. Mod. Phys. **3**, 384 (1931).
[12] A. M. Cravath, Phys. Rev. **33**, 605 (1929).
[13] V. A. Bailey and W. E. Duncanson, Phil. Mag. **10**, 144 (1930).
[14] R. S. Mulliken, Phys. Rev. **40**, 60 (1932).

Note

The Electronic Configuration of Molecules and Their Electron Affinity

IT is well known that the probability of formation of negative ions by electron attachment varies widely for different gases. The cause of this variation, however, has been very obscure. Attempts have been made to relate the electron affinity of a molecule to its dipole moment, but such a hypothesis almost universally breaks down. It is generally held that negative ions may be formed in the so-called "electronegative" gases, but this is largely an ad hoc explanation. It is obvious that the real factor which determines whether or not a molecule will be able to hold a stable additional electron must be closely related to the electronic configuration of the normal molecular state. Heretofore, the data on electron attachment have been of so limited extent that no relation between the electronic structure of a molecule and its electronic affinity could be determined. With the additional evidence which is now available,[1] however, it is possible to point out some extremely interesting relations which appear to exist between the electronic configurations of molecules and their ability to form stable negative ions.

The data which are available for diatomic gas molecules relative to their structure and their electron affinity are given in Table I.

It is seen that the diatomic molecules which are characterized by $^1\Sigma$ configurations ($^1S_0$ for the monatomic gases) do not form stable negative diatomic ions. It is true that negative ions exist in several of these gases, but in such cases they are formed in a dissociation process, one of the products of which attaches the electron. The $^1\Sigma$ state is characterized by having no resultant spin or angular momentum, the electrons all forming entirely closed λ groups. Such a configuration at once makes evident the relative inertness of the molecule with respect to an extra-molecular electron, and negative ions would not be expected to be formed. On the other hand, those molecules which possess uncombined spin or orbital momenta can form stable negative ions by adding an extra electron whose momentum can add to that already present. This rule apparently holds for all diatomic molecules which are available for experiment. It also suggests that certain molecules might tend to form negative ions by attaching electrons in an excited state, providing the life of that state were long enough. Some evidence to this effect has been presented by da Silva[3] for N_2.

TABLE I.

Molecule	Ground state[2]	Negative ion exists
He	$^1S_0$	No
A, Kr, Ne	$^1S_0$	No
H_2	$^1\Sigma$	No
N_2	$^1\Sigma$	No
CO	$^1\Sigma$	No
Cl_2, Br_2, I_2	$^1\Sigma$	No—probably dissociates into Cl^-, etc.
HCl	$^1\Sigma$	No—dissociates into Cl^-
O'_2 (1.62 v)	$^1\Sigma$	No—(probably not)
O_2	$^3\Sigma$	Yes
NH	$^3\Sigma$	Yes
NO	$^2\Pi$	Yes
OH	$^2\Pi$	Yes
CN	$^2\Sigma$	Yes
SO	$^3\Sigma$	Yes

It is possible to extend the reasoning in a limited fashion to polyatomic molecules. It would be expected that highly symmetrical molecules would not form negative ions. This is borne out by experiments in NH_3 and probably by experiments in CH_4. Two particularly interesting cases are presented by CO_2 and N_2O. According to Mulliken[4] these are both linear molecules and have electronic states analogous to the $^1\Sigma$ case for diatomic molecules. The prediction that such molecules would possess no electron affinity is borne out by experiment.[1] The electronic configuration of acetylene, C_2H_2, is of the $^1\Sigma$ type according to Hedfeld and Mecke.[5] It is probable that C_2H_2 has no electron affinity since Loeb found a probability of attachment of the order of 10^{-7} or less, and Tate and Smith[6] in electron bombardment experiments observed negative ions in the gas which were definitely *not* $C_2H_2^-$.

It therefore seems possible that one can predict the qualitative character of the electron affinity of a molecule if the electronic configuration is known. On the other hand, it may be possible to obtain knowledge of the normal state of a molecule from the character of the electron attachment in the gas. This should prove of particular value in studying the electronic structure of polyatomic molecules.

NORRIS E. BRADBURY*
Massachusetts Institute of Technology

[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933). N. E. Bradbury, J. Chem. Phys. **2**, 827 (1934). N. E. Bradbury and H. Tatel, J. Chem. Phys. **2**, 835 (1934). V. A. Bailey and W. E. Duncanson, Phil. Mag. **10**, 144 (1930).

[2] Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 272. University Press, Cambridge, 1932.

[3] M. A. da Silva, Ann. d. Physik **12**, 100 (1929).

[4] R. S. Mulliken, Phys. Rev. **40**, 60 (1932).

[5] Hedfeld and Mecke, Zeits. f. Physik **64**, 151 (1930).

[6] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

* National Research Fellow.

X-Ray Studies of the Molecular Arrangement in Liquids[1]

S. KATZOFF, *Department of Chemistry, The Johns Hopkins University*

(Received September 27, 1934)

An improved technique has been developed for taking x-ray diffraction photographs of weakly absorbing liquids. Photographs of water, heptane, decane, benzene and cyclohexane have been taken and several hitherto unobserved details have been discovered. The photographs of water have been mathematically investigated by the method of Zernike and Prins, and it was concluded that nearly every molecule has four others around it. No evidence was found either for the definite "quartz-like" arrangement or for the extensive degree of close packing which are postulated by Bernal and Fowler. With the organic compounds there was apparent in every case a striking resemblance of the outer parts of the photographs to electron diffraction photographs of the corresponding vapors. This is in agreement with Debye's prediction and argues for a relatively low degree of periodicity in the liquid structure. It has been shown further that the two outer bands which occur in the photographs of the normal hydrocarbons should appear whenever the molecules of the liquid consist largely of lengths of straight saturated hydrocarbon chain. Some discussion of the structure of the organic liquids has been given. In particular, a theory on the structure of liquid benzene has been postulated and found, using the method of Zernike and Prins, to predict with satisfactory accuracy the observed photograph. The viewpoint which has been found useful in the present discussions is that, to a predominating extent, adjacent molecules in the liquid are held together in very nearly the same manner as in the crystal, while, except for this, the arrangement is random.

INTRODUCTION

IN the interpretation of the x-ray scattering from liquids, different investigators have shown preference for different theories. Without at this place attempting a discussion of their relative merits, it may be pointed out that the physical pictures upon which they are based are not necessarily mutually exclusive. Their relative values must depend on the *quantitative* descriptions of these basic pictures. It appears that there is much to be gained by efforts toward a more quantitative interpretation of the x-ray diffraction photographs.

It is a great pity that much of the technique employed by investigators in the field has been so inferior to what is attainable as to fail to show all but the strongest, innermost bands, and, in some of the earlier work, even to introduce false effects. The outer detail of a picture may be weak merely because of the rapid decrease of the atomic scattering factor and the increasing contribution of the incoherently scattered radiation. For example, when the water picture is corrected for these, the second and third bands are comparable to the first (compare Fig. 3 with Fig. 4).

There are usually two important sources of error in making diffraction studies of liquids:

(a) Scattering from the glass tube or other container is superimposed on that from the liquid itself.
(b) The x-ray beam is not strictly monochromatic, but has a background of continuous radiation, the scattering of which is superimposed on that of the monochromatic rays.

In the present work they have been avoided by

(a) using a flowing cylindrical jet of the liquid, and
(b) using a rocksalt crystal monochromator.

APPARATUS AND TECHNIQUE

A vertical section of the camera (effective film diameter = 57.3 mm) and circulating system is shown in Fig. 1. A motor with reducing gear by compressing and releasing the rubber bulb *A* alternately fills the glass bulb *B* through the lower valve and empties it through the upper valve. The float valve serves to regulate the flow, always keeping a certain minimum amount of liquid around it. In order to make pictures of liquids at other than room temperature, these parts were made small enough to be enclosed completely in a 1-quart Dewar vessel, and the remainder of the circulating system was made with Dewar insulation (double walled, silvered and evacuated). As little as 20 cc of liquid can be circulated in this system. The liquid jet is 0.66 mm in diameter.

[1] Adapted from the dissertation submitted by the author to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

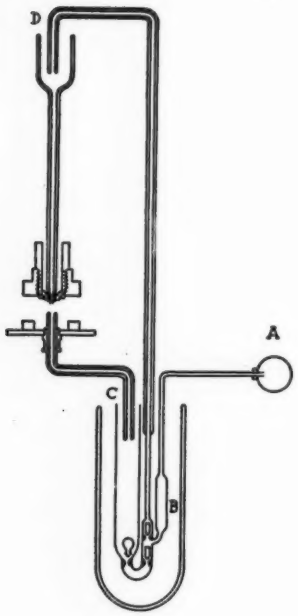


FIG. 1.

The film holder is a brass collar which can be strapped on to the camera, a rubber edging on the collar serving to make the joint air- and light-tight. Aluminum foil, 0.025 mm thick was always used over the film.

Copper $K\alpha$ radiation was used, obtained from a Seemann hot-filament x-ray tube[2] operating at 20 m.a. and 45 kv peak. In order to get effectively monochromatic radiation, the very compact Seemann monochromator-slit system was used, which contains a small excellent rocksalt crystal set for the (200) reflection. It was later found that the intensity of the reflections could be about doubled, without causing appreciable broadening, by polishing the crystal face,[3] so a polished crystal was used in all subsequent work.

A special design for the filament in the x-ray tube was used in this work in order to secure a uniformly intense beam through the slit. This is a problem which becomes important when a crystal monochromator is used, for, if the part of the focus which serves as the source of x-rays is not uniform, the sample will be exposed to a beam of corresponding non-uniformity. If there is appreciable absorption in the sample, this can cause considerable error in the relative intensities at different parts of the photograph; Möller and Reis's absorption corrections,[4] which were used in this work, are based on the assumption of a uniform, parallel beam. The filament is shown in Fig. 2. It is made by winding the

FIG. 2.

tungsten wire between the teeth of a small comb, specially made for the purpose, of small strips of thin sheet iron. In mounting the filament there was placed over the focusing tube a flat metal disk having a small rectangular hole into which the filament protruded. The effect is that of a flat surface, a small rectangular section of which emits electrons. The electrons move perpendicular to this surface, producing a small rectangular focal spot, which appears like a diffuse projection of the filament itself. Pinhole photographs showed very excellent spots, and films placed where the sample should be showed that the beam coming through the slit was very uniform.

It was found that the darkening which occurs on the films in the region of very small angular deviation could be avoided, for the most part, by replacing the air in the camera by a gas of less scattering power. A slow stream of helium was passed through the camera for this purpose, hydrogen not being used since it appeared to fog the films due to its reducing properties. For taking photographs of liquids at low temperatures, it was found necessary to dry the gas with phosphorus pentoxide and to close off *C* and *D* in order to avoid the condensation of ice on the liquid. For liquids near the boiling point it was found necessary to increase the rate of flow of the helium in order to sweep out the vapors. Even so, these pictures of hot liquids showed considerable darkening at small angles, and it is not certain whether this is purely the tempera-

[2] Purchased from the Seemann Laboratory, Freiburg i. Br.

[3] Others have observed similar effects. An example is given in Bragg and Bragg, *X-Rays and Crystal Structure*, p. 219, 1924. (London, G. Bell and Sons, Ltd.)

[4] H. Möller and A. Reis, Zeits. f. physik. Chemie **A139**, 425 (1929).

ture effect or whether an appreciable part of it was due to scattering by the vapor surrounding the jet. Considerable evaporation from the jet occurred in these cases, sometimes amounting to as much as 20 cc of liquid per hour. In order to conserve the substance, traps were inserted in the outgoing gas line.

The time of exposure was variable, depending on the purpose of the exposure. Ten hours sufficed for the weak, outer parts of the photographs. A set of comparison spots, made by exposing small sections of a strip of film for measured lengths of time, was made for every photograph and developed simultaneously with it. The films were photometered with a Moll microphotometer. As a rule, for all but the inner part of the film, a 5-mm horizontal strip of the film was photometered, in five 1-mm sections, the five curves being superimposed on the same piece of sensitized paper. For the inner part of the film, where the bands have appreciable curvature, a 3-mm strip was taken. This method of minimizing the effect of grain irregularities is simpler than the method of Richtmyer and Hirsch[5] (in which the film is constantly oscillated) and quite as effective.

Materials

The liquids studied in this work were water, benzene, cyclohexane, normal heptane and normal decane. Some of the cyclohexane which was used was obtained from the Eastman Kodak Company, and some was made by the author by the catalytic hydrogenation of benzene. The two samples had the same refractive index and gave identical pictures. Both the heptane and the decane, which were of over 99 percent purity, were very kindly supplied by the American Petroleum Institute from their supplies at the Bureau of Standards.

Study of Water

In the case of water it was possible to check some of the results against a very similar, careful piece of work by Meyer,[6] who, also using a free jet and a crystal monochromator, took photographs of water between 3° and 40°. Amaldi[7] has also tried a crystal monochromator but, although he reports little advantage over the use of low voltage, filtered radiation, his published intensity curves differ somewhat from those of Meyer or of the present writer.

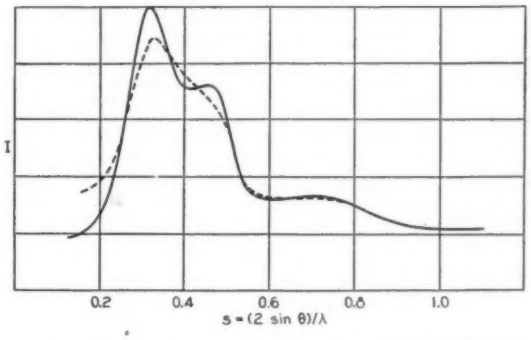


FIG. 3. Intensity curves for water at 3° (full line) and at 90° (dotted line). Corrected for absorption and polarization.

Pictures of water were taken at various temperatures between 3° and 90°. The intensity curves for the two extremes are given in Fig. 3.

Existing discussions of the water photograph

There are to be found in the literature a number of interpretations of the x-ray diffraction from water. First, it has been frequently pointed out that the position of the first band is in agreement with the hypothesis of a rough close packing of spherical molecules, the Keesom[8] relation being applied. Meyer, who first observed the second band, explained its appearance by pointing to the prevailing conception of water as an associated liquid. The disappearance of the second band with rise in temperature (which can be better described as a decrease in the intensity of both maxima and an increase in intensity between them) was correspondingly interpreted as due to the decrease in association. This interpretation was substantiated by the fact that the addition of salts, which should also break up association, had the same effect. Stewart, suggesting that "cybotaxis" should replace "association," explained the bands by postulating the existence of rough "planes," pointing out that the two strongest lines in the picture of powdered ice were not far from

[5] F. K. Richtmyer and F. R. Hirsch, Jr., Rev. Sci. Inst. **4**, 353 (1933).
[6] H. H. Meyer, Ann. d. Physik **5**, 701 (1930).
[7] E. Amaldi, Phys. Zeits. **32**, 914 (1931).
[8] W. H. Keesom, Physica **2**, 718 (1922).

the first two bands in the picture of water. The change in the photograph which occurs with rise in temperature he correspondingly explained as follows: "With temperature increase, the nature of the group changes, one set of planes becoming more poorly defined because of more slippage and less orderly arrangement. The alteration in grouping is also shown by the decrease in distance between planes."[9] This last sentence refers to the anomalous *outward* movement of the first band with rise in temperature.

There is, finally, the paper by Bernal and Fowler[10] which appeared about the time the present calculations were begun. As a starting point, they use the formula given by Zernike and Prins[11] for coherent x-ray scattering by an atomic liquid:

$$I(x)=KPF^2(x)\left\{1+\mu\int_0^\infty 4\pi r^2[\rho(r)-1]\times(\sin xr/xr)dr\right\} \quad (1)$$

where r is the distance, in Angstroms, from the center of an atom.

$\rho(r)$ is the average density of atomic centers at distance r from the center of an atom. It is in arbitrary units; $\rho=1$ corresponds to the average density throughout the liquid.

μ is the reciprocal of the atomic volume of the liquid, in atoms per cubic Angstrom.

$x=(4\pi \sin\theta)/\lambda$, where λ is the wave-length of the x-rays, in Angstroms, and θ is half the scattering angle.

$F(x)$ is the atomic scattering factor for the given value of x.

$I(x)$ is the contribution of the coherently scattered radiation to the total intensity for the given value of x.

P is the polarization factor $(1+\cos^2 2\theta)/2$ when unpolarized x-rays are used, or $(1+0.723\cos^2 2\theta)/2$ when using Cu $K\alpha$ x-rays reflected from a rocksalt crystal.

K is a constant.

[9] G. W. Stewart, Phys. Rev. **35**, 1426 (1930).

[10] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933). The author wishes to acknowledge the influence of this paper in the following discussion.

[11] F. Zernike and J. A. Prins, Zeits. f. Physik **41**, 184 (1927).

By postulating a water structure somewhat analogous to the structure of quartz, and modified by some close packing, they synthesized a density function $\rho(r)$ which led, using this formula, to an intensity distribution curve resembling that of Fig. 3 except that the second maximum was much too weak. It may be pointed out that an examination of the density functions (p. 520 of their article) by which they represent the "quartz-like" structure and the "close packed" structure shows a great deal of arbitrariness in the selection of these functions. It is felt, therefore, that their choice of wording was perhaps unfortunate in its emphasis of the analogy to the crystalline structures.

The calculations to be presented here are more direct. Zernike and Prins[11] showed that, by a simple application of the Fourier integral theorem, the above equation could be solved for $\rho(r)$:

$$[\rho(r)-1]=\frac{1}{2\mu\pi^2}\int_0^\infty x^2[E(x)-1]\frac{\sin rx}{rx}dx, \quad (2)$$

where

$$E(x)=I(x)/KPF^2(x).$$

The absolute value of I is not known in these experiments. E, however, is determined by placing it equal to unity for large values of x, since the value of the integral in (1) approaches zero with increasing x. Debye and Menke[12] have already applied this formula to obtain the ρ-function for liquid mercury and liquid gallium. Amaldi[7] actually tried it for water but, upon getting a geometrically impossible ρ-function, concluded that there is too much "relative orientation" of the molecules in water for the method to be applicable.

Sources of inaccuracy

There are, indeed, several reasons why it is much more difficult to apply in the case of water than in the case of mercury or of gallium, the trouble lying in the accurate determination of the E-function. To begin with, the contribution of the incoherently scattered radiation to the total intensity is far more important in the case of a light compound like water than in the case

[12] P. Debye and H. Menke, Phys. Zeits. **31**, 797 (1930); H. Menke, Phys. Zeits. **33**, 593 (1932).

of these heavy metals. Thus, for water, the incoherent scattering is about half the total at about $x=5$. There is, in addition, the fact that the F-curves for the lighter elements fall off so rapidly with x that small inaccuracies in the I-curve are much magnified in the E-curve. It might be pointed out further, in this connection, that the F-curves are less accurately known for the light elements than for the heavy ones. There is also the fact that the experimental intensity curve extends to only a finite value of x whereas the integral must be extended to infinity. Meyer used molybdenum radiation in addition to copper radiation, making available for these calculations a part of the curve somewhat past that shown in the figure. The remainder of the curve must be considered, for the purpose of these calculations, to be flat. There is, finally, the difficulty to which Amaldi referred, namely, that in using the factor F_{H_2O} it is assumed that the liquid consists of H_2O units in which the electron distribution has spherical symmetry. Accordingly, the formula is not so correctly applicable in the case of water as in the cases which Menke investigated. Nevertheless, it is felt that the lack of rigor introduced by this is not more important than the practically unavoidable difficulties mentioned above. For, firstly, if the structure of water resembles that described in the work of Stewart, Bernal and Fowler, or the present writer, the structural unit may be considered, in place of a bent H_2O molecule, as an oxygen atom approximately tetrahedrally surrounded by four half-hydrogens, the electron distribution of which is much more nearly spherical. Moreover, the effect of the dissymmetry due to the hydrogens would be small except at small angles.

It would appear, then, that the accuracy of the E-curve, as worked out purely from experimental data, leaves much to be desired. There exists, however, an important criterion for the correctness of an E-curve, namely, that the ρ-function calculated from it must be zero for all values of r less than the atomic diameter. The problem, accordingly, consists of finding an E-curve which (a) leads to a ρ-function which is approximately zero for $r<2.5$A, and (b) within the limits of uncertainty explained above, corresponds to the experimental intensity curve.

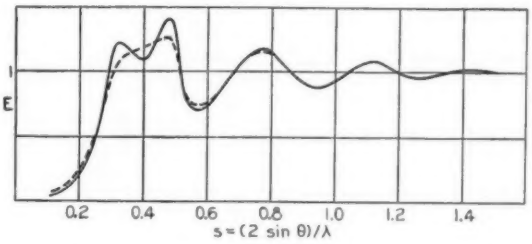


FIG. 4. E-curves for water at 3° (full line) and at 90° (dotted line).

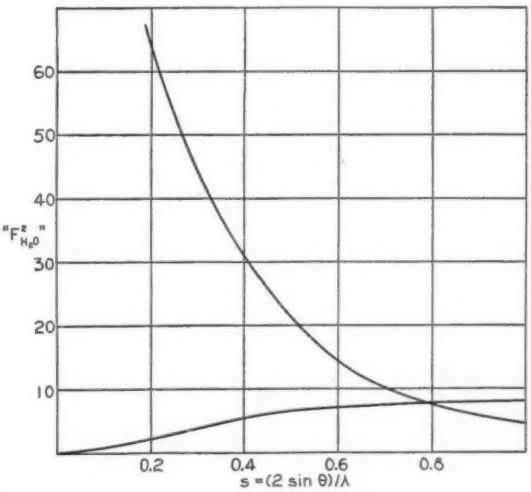


FIG. 5. Coherent and incoherent scattering by water. Incoherent scattering calculated for $\lambda=1.54$A.

Fig. 4 shows the curve adopted. It fulfills the first condition quite satisfactorily—ρ does not differ from zero by more than 0.25 near $r=0.5$A and by more than 0.05 near $r=2$A. This is approximately the tolerance allowed in Menke's work also. Concerning the second, it corresponds to Fig. 3 when using the curves for incoherent and coherent scattering shown in Fig. 5. The curve for incoherent scattering was calculated by applying the modified Wentzel formula[13] to the f-values for H and O given by James and Brindley.[14] The curve for $F^2_{H_2O}$ is almost exactly the same as that of James and Brindley for $O^=$.

We have, of course, no way of proving that the curve which was adopted is the correct one, or the only possible one; it seemed, however, during the course of the trials which led to it, that any curve which satisfies the two conditions

[13] E. O. Wollan, Rev. Mod. Phys. **4**, 206 (1932).
[14] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

stated above must differ but slightly from the curve adopted.

Technique of the Calculations

The integrations were performed graphically, using a thin graph paper. A set of $\sin rx/rx$ curves was prepared, each on a separate sheet, for values of r differing by 0.2A. On another sheet was constructed the $x^2[E(x)-1]$ curve. By placing one sheet on the other, with a third sheet above, taking care to have the rulings coincide, and placing upon a glass plate illuminated from below, corresponding ordinates of the two curves could be readily picked out and their products plotted directly on the upper sheet. The area under this third curve is proportional to the desired integral. Where a harmonic analyzer is available, the work can be performed in much less time and with much less tedium.

The Structure of Water

The ρ-function for water at 3°, calculated in the manner described above, is plotted in Fig. 6. The first peak occurs at about $r=2.9$A and the following maximum is at $r=4.5$A. The first two minima are at $r=3.4$A and at $r=5.7$A. The value of $\int 4\pi r^2\rho(r)dr$ extended under the first peak (as far as 3.4A) corresponds very nearly to four units; i.e., *each oxygen atom has, on the average, about four nearest neighboring oxygens.*

It is, of course, to be realized, in seeking to visualize a structure of water which is in agreement with the ρ-curve, that the information given by the curve is of a rather indefinite nature. For example, it does not tell whether every oxygen has four nearest neighbors, or whether some have three while others have five, nor does it tell the relative orientations of these oxygens. It is apparent, however, that it is possible to describe in a rough way a simple and reasonable structure which seems in agreement with the curve. For if, in water, each oxygen is surrounded by four others, not in a tridymite-like (tetrahedral), or quartz-like, or, indeed, in any very regular manner, the corresponding ρ-curve would have the characteristics of that which has been calculated, and the density of water would be very close to that which is observed. (Fig. 7 shows approximately the ρ-curve of Bernal and Fowler. There is only a suggestion in the present results of the strong maximum at $r=4$A which is due to their postulated quartz-like structure.)

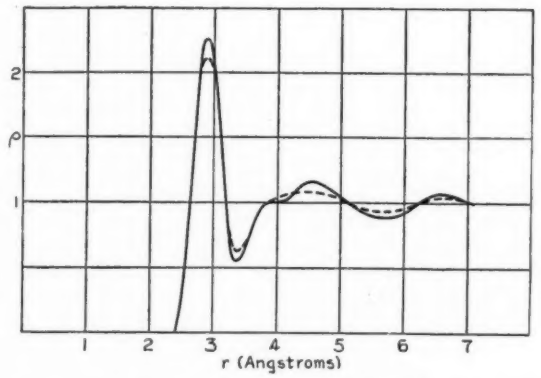


Fig. 6. ρ-curves for water at 3° (full line) and at 90° (dotted line).

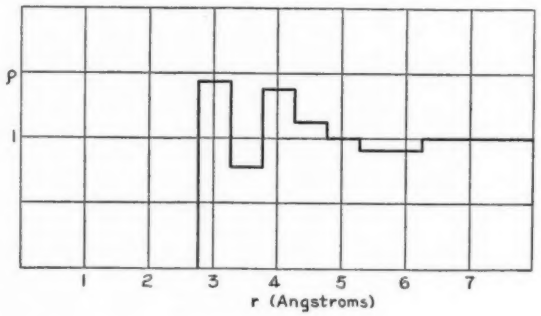


Fig. 7. Bernal and Fowler's ρ-curve for water at 3°.

What has been described here is, in the most general terms, merely a broken down ice structure. In ice it appears that each oxygen is tetrahedrally surrounded by four others, with the hydrogens on or near the center lines between adjacent pairs of oxygens.[15] If water had a structure in which each oxygen were tetrahedrally surrounded by four equidistant hydrogens and each hydrogen were on the center line between a pair of oxygens, but in which there were otherwise random orientation about the hydrogen bonds (comparable to vitreous silica), the ρ-curve would have a very strong peak at $r=4.5$A and would be very low in the region

[15] Peculiarities in the crystallography of ice and in the dielectric properties are probably to be ascribed to the anomalous properties of the hydrogen bond between oxygens rather than to an essential error in this picture.

between the two peaks. Now, although the ρ-curve has a maximum at $r=4.5$A, it is not nearly so sharp nor so strong as it would be for the above case, and between the two peaks it has only a narrow minimum instead of being nearly zero over the whole range. The most obvious modification of the above picture in order to account for the differences in the ρ-curve and also to account for the density is to suppose that the O–H–O angle is not necessarily 180° but can have any value between 180° and, say, 150°. (Or, since the scattering of x-rays by hydrogen is neglected, an equivalent supposition is that the H–O–H angles are now no longer the tetrahedral angle (109.5°). Both effects probably exist.)

In this development, for simplicity of the visualization, the hydrogens were considered as equally held between pairs of oxygens. If, as seems more nearly true, definite H_2O units exist, the description must be given as follows: The molecule may be considered as a tetrahedron, the oxygens being at the center, positive charges (hydrogens) at two of the vertices, and concentrations of negative charge (electrons) at the other two vertices.[10] Then the liquid is considered to have a continuous structure, in which each hydrogen of a molecule is in close proximity to one of the concentrations of negative charge in another molecule, while, except for this, there is no very distinctive relative orientation of the molecules.

A ρ-function corresponding to the x-ray photograph of hot water (90°) was separately worked out (Fig. 6). The essential difference between it and the one for cold water is that the outer details are about half as pronounced. The size of the first peak is not noticeably different. Thus, the predominating feature of the arrangement at 90° is still the four-coordination, although the randomness is otherwise greater than at 3°.

The decrease in the density of water on approaching the freezing point may be due to some peculiar arrangement which exists to too small an extent to show on the photographs. It seems more reasonable, however, to suppose that it is due merely to the increasing tendency for the O–H–O angles to approach 180° as the heat motion becomes less violent.

It is of some interest to inquire whether the ρ-curves of Fig. 6 and the above interpretations support, or are compatible with the theory of cybotaxis. The question would appear difficult to answer in view of the difficulty in constructing and examining three-dimensional models which would correspond to the curves. To the present author, however, it appears likely, in view of the lack of sharpness of the maxima and minima in the ρ-curves beyond the first, that cybotactic planes can have no very clear existence in the arrangement. It is believed that there is little, if any, distinct periodicity, and, in any case, it should be considered as incidental; the characteristic of the structure which is mainly to be stressed is the relative arrangement of nearest neighbors.

Study of *n*-Heptane and *n*-Decane

Photographs were taken of normal heptane at $-50°$ and at 80°. A comparison of the intensity curves (Fig. 8) illustrates the typical temperature effects—inward displacement and broadening of the strong band and increase in intensity at small angles. The first band is well known, appearing in nearly the same position for all the liquid normal paraffins and higher alcohols. The two outer maxima, at $s=0.46$ and at $s=0.81$ had not been observed before for *n*-heptane, so it became a matter of great interest to determine whether, like the first maximum, these were also to be found with the other liquid normal paraffins. Accordingly, some *n*-decane was procured and a picture taken, at room temperature, the picture turning out to be practically identical with that of *n*-heptane. It appears, however, that this observation is not altogether a new one. When Stewart reported the x-ray scattering from the normal paraffins, he mentioned the appearance of both of these outer bands in the cases only of tetradecane and pentadecane, but seemed uncertain as to whether the accuracy of the experiments warranted their recognition. More recently, electron diffraction work[16] has shown that these two outer maxima also occur in the pictures of various oils.

The first band has already been thoroughly discussed in the literature. It is characteristic of closely packed parallel hydrocarbon chains. Concerning the third maximum, at $s=0.81$,

[16] L. R. Maxwell, Phys. Rev. **44**, 73 (1933).

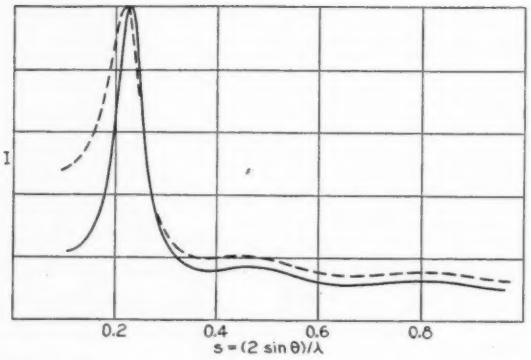


FIG. 8. Intensity curves for *n*-heptane at −50° (full line) and at 65° (dotted line). Corrected for absorption and polarization.

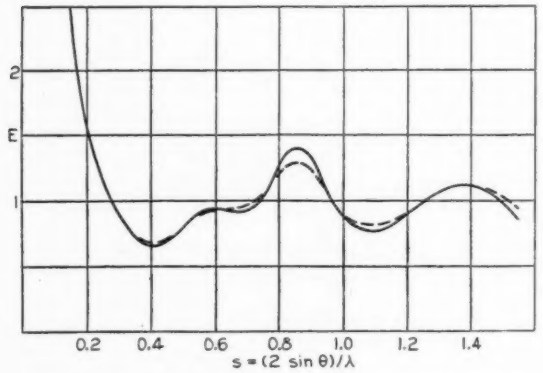


FIG. 9. Calculated *E*-curves for gaseous $C_{14}H_{30}$ (full line) and C_5H_{12} (dotted line).

Stewart has noticed that the corresponding interplanar distance, as calculated from Bragg's law, is about equal to the periodicity of the carbon atoms in the direction of the hydrocarbon chain axis, so he has correspondingly suggested that the molecules are arranged in such a manner as to form planes of carbon atoms perpendicular to the direction of the molecule axis.

There is, however, a matter of great importance not mentioned in the above, namely, that the two outer maxima are in the same positions as the maxima observed by Wierl[17] in his electron diffraction pictures of gaseous normal paraffins. Wierl took pictures only of *n*-pentane and *n*-hexane, but it is apparent from the theory of x-ray scattering by gases that the higher ones would have the same characteristics. (Fig. 9 shows calculated *E*-curves for plane zigzag chains of five and fourteen carbons, where the C–C distance is 1.54A and the angles are 109.5°; the two curves are almost identical.) In fact, these maxima would appear whenever we have molecules consisting largely of lengths of saturated hydrocarbon chains, as in the case of the oils which Maxwell investigated. This recalls Debye's conclusions that only the inner bands are to be ascribed to intermolecular arrangement, while the outer details are the same as those of the gas.[18] Accordingly, the facts would seem to suggest that, except for the parallel orientation of the molecules, there is extensive disarrangement in the liquid. The recent calculations of Warren are fully in accord with this view.[19]

[17] R. Wierl, Ann. d. Physik **8**, 521 (1930).

STUDY OF BENZENE

Photographs of benzene were taken at 8° and at 65°. The typical temperature effect is again apparent in the comparison of the two intensity curves (Fig. 10). All of the bands in the benzene picture have been observed before without the use of a crystal monochromator, although not all, apparently, by any one observer.

There is in the literature some discussion of the benzene picture. Stewart[20] supposes that in liquid benzene the structure is characterized by the parallel orientation of flat benzene rings, and the distance between the rough planes so formed is given, using Bragg's law, by the position of the first, strong band. This gives the interplanar distance, or the thickness of the ring, as 4.7A. Katz[21] is more concerned with the weak band just outside the strong one and calculates from it, also assuming parallel orientation of the rings, the thickness of the rings to be about 3.6A. The first band is, then, to be explained by using Keesom's equation, assuming that the packing is mainly a random one. Eastman[22] has been tempted to compare the x-ray picture of the powdered solid with that of the liquid. The agreement is not good. The

[18] P. Debye, M. I. T. J. Math. and Physics **4** (1925).
[19] B. E. Warren, Phys. Rev. **44**, 969 (1933). In fact, from the point of view of his calculations, had he not neglected the inner details when subtracting the $4\pi r^2\rho$ curve from the *g*-curve (p. 971 of his article) he would have been in position to predict the two outer bands.
[20] G. W. Stewart, Phys. Rev. **33**, 889 (1929).
[21] J. R. Katz, Zeits. f. angew. Chemie **41**, 329 (1929).
[22] E. D. Eastman, J. Am. Chem. Soc. **46**, 917 (1924).

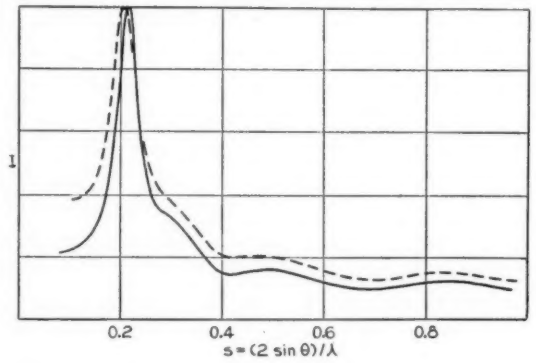


FIG. 10. Intensity curves for benzene at 8° (full line) and at 65° (dotted line). Corrected for absorption and polarization.

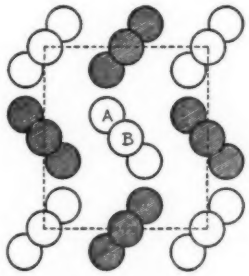


FIG. 11. The unit cell of benzene (orthorhombic); $a=7.44$A, $b=9.65$A, $c=6.81$A. The hatched molecules are half the b distance below the plane of the others.

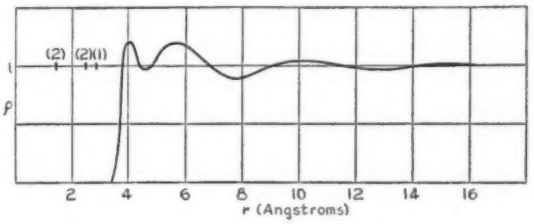


FIG. 12. ρ-curve for benzene.

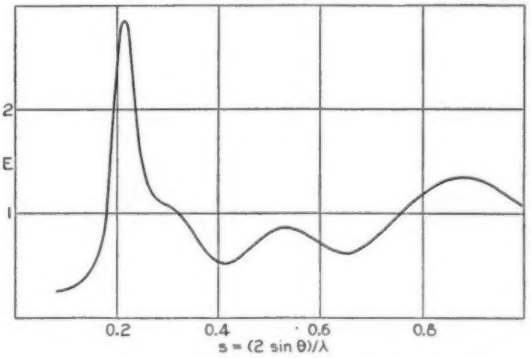


FIG. 13. E-curve for benzene as calculated from the ρ-curve of Fig. 12.

position of the strong band in the liquid picture differs from that of the strongest powder line by about five percent, the powder line corresponding to the *larger* spacing, whereas the implied looseness of the liquid structure should require the opposite. There is no striking resemblance at all between the remainders of the photographs.

The calculation of the ρ-function from the x-ray diffraction photograph by means of Eq. (2) is subject to the same difficulties which were discussed for the case of water and which, in fact, enter here to an even greater extent. It was accordingly thought more desirable to proceed from the opposite direction; i.e., by hypothesizing that the influences which determine the crystal structure still exist in the liquid extensively enough to determine roughly the relative arrangement of adjacent molecules (the idea here being similar to that with water), to prepare a ρ-function and see if it led, by Eq. (1) to an E-curve in agreement with the experimental curve. In Fig. 11 is shown the unit cell of crystalline benzene, as determined by Cox.[23] It is admittedly not in thorough agreement with the observed intensities of reflections and, in addition, suffers from the defect common to many organic crystal structure determinations, that the positions of the hydrogens, which are of major importance in the molecular arrangement, are mainly to be inferred from the positions of the carbons. An examination of this structure shows that carbon atoms like "A" have six neighbors at a distance of 3.85A, four at 4.10A, and four at 4.35A, while atoms like "B" have four at 3.85A, four at 3.95A, two at 4.20A, and two at 4.35A. The prominence of C–C distances of about 3.9A is very striking. Without proposing a detailed theory of the liquid structure, one may suppose that the crystal forces still exist in the liquid extensively enough to preserve this prominence of the smallest C–C distance.

It was remarkable that the first ρ-curve which was tried gave essentially the desired result. Fig. 12 shows the finally adopted curve, which differs only in minor details from that which was first tried. The peak at $r=4$A corresponds to an

[23] E. G. Cox, Proc. Roy. Soc. **A135**, 491 (1932).

average concentration of about eight atoms at this distance. The value of r (5.5A) for the position of the next peak was taken as the average distance between other than adjacent carbons of neighboring molecules (adjacent carbons being already represented in the first peak). In Fig. 13 is shown the E-curve which was calculated from this, and which corresponds (using James and Brindley's table for F_C) with the experimental intensity curve.

Incidental items of the calculations

While recognizing that relations between the ρ- and E-curves exist, in a rigorous sense, only between their wholes, it became apparent, during the calculations with benzene, that the following relations between certain of their characteristics could be more or less definitely identified:

(a) The first, strong peak of the E-curve is associated mainly with the strong maximum in ρ at $r=5.5$A, the minimum which follows it, and the minimum between $r=3$A and $r=4$A. A similar sequence of nearly equally spaced maxima and minima would be characteristic of any liquid having small molecules relatively widely separated. This is apparently the foundation for Keesom's relation.

(b) The bulge at the bottom of the first strong peak of the intensity curve is due to the sharp rise in ρ at $r=4$A. It could appear in approximately this position whenever there exists in the liquid a predominance of interatomic distances of about 4A. One can, accordingly, explain the fact that Katz has observed it in the photographs of many simple benzene derivatives by suggesting that there is a tendency for this feature to be preserved in any arrangement of benzene rings.

(c) The two outermost maxima are due to the atoms at $r=1.42$A, 2.48A, and 2.84A, the interatomic distances within the molecule itself. The second of these maxima is in the same position as the one found by Wierl for the gas.[17] The first, however, is at a slightly larger value of s than is the corresponding maximum of the gas picture. It became clear, however, during the above calculations, that this shift is an effect of the remainder of the ρ-curve; this value of s is not so large that the intermolecular arrangement is negligible. It may be noticed, however, that in the higher temperature picture, the minimum which precedes it is weaker and there is a corresponding shift of this maximum toward that of the gas.

Rumpf[24] has also observed the outermost maximum, in the same position (although his curve shows a much narrower and sharper peak than does the one here given). He has calculated from its position that the C–C distance in benzene is 1.36A. The question here is mainly what F-curve to use. The calculations were repeated, using James and Brindley's more recent curve, which falls off much less rapidly in this region than does the curve used by Rumpf, and also taking into account the slowly rising curve for the incoherent scattering. A distance of 1.42A was found to be in closest agreement with the observed position of the maximum.

Study of Cyclohexane

Diffraction photographs were taken of liquid cyclohexane at 8° and at 65°. The intensity curves are given in Fig. 14. The first band seems to be the only one as yet mentioned in the literature. Because of its sharpness, the effect of the finite width of the jet on its shape was investigated. The effect was, however, found to be small, the correction being, for the low temperature picture, an increase in peak intensity of about five percent and the same decrease in width. The third and fourth maxima are in approximately the same positions as those found by Wierl in the electron diffraction from the gas.

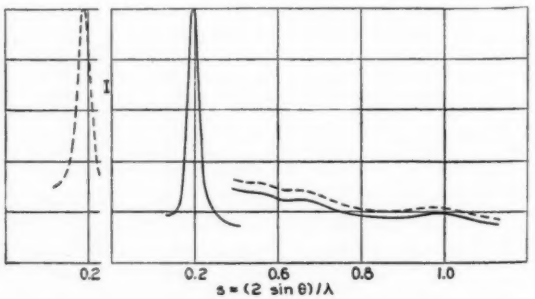


FIG. 14. Intensity curves for cyclohexane at 8° (full line) and at 65° (dotted line). Corrected for absorption and polarization. The ordinate scale for the outer parts of the curves is doubled.

[24] E. Rumpf, Ann. d. Physik 9, 704 (1931).

The crystal structure of cyclohexane is not known. Hassel and Kringstad[25] have, however, shown it to be cubic ($a_0=8.41$A, four molecules in the unit cell) and have shown its space group to be probably T_h^2 or O_h^4. This is of some interest in view of the general belief that the liquid structure is characterized by parallel orientation of the rings, the thickness of the ring being, from the position of the strong band, about 5.1A. Since the arrangement cannot be of such a type in the crystal, since it is cubic, it is very probable that there is no great tendency for parallel orientation in the liquid either.

The Solution of Cyclohexane and Benzene

Ward[26] has found that in the x-ray scattering from a solution of cyclohexane and benzene, the two main peaks for the pure components were both present. The simplest explanation, which he presented, is that we have here, not a random distribution of the two kinds of molecules, but an emulsion of one liquid in the other. It may be pointed out that, even if we accept an explanation of this nature, it is unnecessary to assume the existence of aggregates so large that "emulsion" is more applicable than "association." If we should assume the existence in the solution of aggregates of only a few (hardly more than ten) cyclohexane molecules, arranged as in pure cyclohexane, calculations such as have been presented in this paper would undoubtedly be in accord with the experimental observation. The carbon atoms in the interior of the group would be surrounded very nearly as in the pure liquid; the atoms at the surface of the group would be less nearly so surrounded; it appears not at all unreasonable to suppose that the average ρ-function for the carbon atoms of such a small aggregate would sufficiently resemble the ρ-function for pure cyclohexane to account for the appearance of an intensity maximum in approximately the same position as the strong band of the pure liquid.

The author acknowledges with pleasure his debt of gratitude to Dr. Emil Ott for suggesting this work and for his aid during its progress.

[25] O. Hassel and H. Kringstad, Tidsskrift f. Kjemi og Bergvesen **10**, 128 (1930); C. A. **25**, 1500 (1931).
[26] H. K. Ward, J. Chem. Phys. **2**, 153 (1934).

DECEMBER, 1934 JOURNAL OF CHEMICAL PHYSICS VOLUME 2

The Ultraviolet Absorption of Methane

A. B. F. Duncan and John P. Howe, *Department of Chemistry, Brown University*

(Received October 1, 1934)

The absorption spectrum of methane from 1450A to 850A is found to be entirely continuous and all excited states up to the first ionization potential are repulsive.

THE absorption spectrum of methane in the Schumann region was photographed first by Leifson[1] using a small vacuum grating spectrograph and an uncondensed discharge in hydrogen as a continuous source. He found six bands at low pressures all below 1558A. Rose,[2] using the same source and a small prism instrument, was unable to find these bands, and suggested that Leifson's bands were merely gaps in the band spectrum of hydrogen, which appears with great intensity in such a source. The object of the present work was to photograph the spectrum under greater dispersion and resolving power, using a source which gave a true continuum in the region in question and to extend the spectrum to shorter wave-lengths, below the Schumann region.

[1] S. Leifson, Astrophys. J. **63**, 87 (1926).
[2] A. Rose, Zeits. f. Physik **81**, 758 (1933).

Experimental Procedure

The methane was prepared by the Grignard reaction, from purified methyl iodide, especial precautions being used to free the gas from ether vapor. The methane was fractionated in vacuum, the middle fraction only being used. It was admitted to the spectrograph from a storage bulb through small calibrated volumes.

The one meter focus glass grating had 125,000 lines, ruled 30,000 to the inch. The dispersion was 8.52A/mm in the first order and the resolving power unusually high for a small instrument, since care was taken to cover all the ruled surface with light. The spectrograph was evacuated with a single Cenco Hypervac pump, which proved entirely adequate down to about 1000A. Below this, absorption by hydrogen diffusing through the slit from the discharge became troublesome, and below 850A absorption by this gas became complete.

The light source was a condensed discharge in hydrogen, used by many workers in this region. An 8 mf. condenser, charged to 3000 volts, was discharged twice a second through a one millimeter capillary tube. A strong continuum was obtained, with lines of Si, C, O and B superimposed. Exposure times were four to ten minutes.

Results

Exposures were made at methane pressures from 0.002 mm up to 1.0 mm. The absorbing column was about two meters. At the lowest pressure the methane absorption was barely perceptible, extending from about 1300 to 1200A. As the pressure was increased the absorption widened rapidly on the short wave side and slowly on the red side. At our highest pressure the absorption extended to about 1450A but no significance was attached to any of these limits. It is quite possible that we could have observed absorption up to 1800A (as reported by Leifson at atmospheric pressure) by going to still higher pressures.

In no case was any indication of vibrational structure in the absorption obtained. With our spectrograph, any vibrational structure should be clearly resolved, and the rotational structure partially resolved or at least indicated. So we believe that it may be safely concluded that in this region of the spectrum, methane shows only true continuous absorption.

The ionization potential of methane is 14.5–15.2 volts[3] (855–810A). Most of the continuous absorption observed by us cannot thus be due to the usual continuum following a Rydberg series, but must be due to repulsive electron states. Furthermore we must conclude that all of these excited states are repulsive up to ionization.

Without a detailed examination of the wave functions for the excited states, we can only speculate on the reasons for the instability of methane on electronic excitation. According to Mulliken,[4] the lack of discrete absorption in methane is to be explained by the high value of its ionization potential, as compared with that of ammonia, which shows discrete absorption at considerably longer wave-lengths. It is the opinion of the present writers that the value of the ionization potential is not so important as the value of the lowest excitation potential. This is much higher in methane than in ammonia, if the absorption at the lowest pressure in each case comes from molecules in the $n''=0$ level of the normal state of the molecule. The larger excitation energy required in methane might remove an electron (probably an a_1 electron) so far that its bonding power would be entirely lost. It would then be impossible to form four bonds (without the promotion of one of the inner electrons) and dissociation would occur.

Several examples of continuous ultraviolet spectra of molecules having tetrahedral symmetry are known and the phenomenon may be a general one. Lead tetramethyl, observed by one of us,[5] carbon tetrachloride[1] and germane, GeH_4[6] are examples.

---

[3] G. Glockler, J. A. C. S. **48**, 2021 (1926).
[4] R. S. Mulliken, J. Chem. Phys. **1**, 501 (1933).
[5] Duncan and Murray, J. Chem. Phys. **2**, 636 (1934).
[6] Observations by Mr. H. E. Mahncke in this laboratory.

Entropy and the Absolute Rate of Chemical Reactions

I. The Steric Factor of Bimolecular Associations

O. K. RICE AND HAROLD GERSHINOWITZ, *Chemical Laboratory, Harvard University*

(Received September 7, 1934)

The equilibrium constant for a bimolecular association may be expressed in terms of the energy change, ΔE, and standard entropy change, ΔS°, on association. On account of the well-known relation between the equilibrium constant, and the rate constants of the bimolecular association and its reverse, the corresponding unimolecular decomposition, the values of these rate constants could be determined separately, if one could divide each of the terms, ΔE and ΔS°, into two parts, in the proper way. The proper method of dividing ΔE is known; this paper is concerned with the division of ΔS°. Considered from a statistical point of view, the entropy of a system depends upon the volume in phase space available to the system under fixed thermodynamic conditions. The separate rate constants will depend upon the fraction of the phase space in which it is possible for the reaction under consideration to take place. Application of this principle leads to an interpretation of the collision number and the steric factor of bimolecular association reactions. The known bimolecular associations have been discussed from this point of view.

INTRODUCTION

IN a recent interesting paper Rodebush[1] has shown that it is possible to get considerable information about the kinetics of a reaction from the statistical expression that gives the equilibrium constant in terms of the entropies of the reacting substances. The rôle that the entropy plays in determining the rate of reaction is readily appreciated when we remember that the antilogarithm of the entropy of a system is proportional to the volume of the phase space, or to the number of stationary states, in which the molecules of the system can exist,[2] and that the rate must depend upon the fraction of the states in which reaction may occur. Essentially this principle has been stated by Rodebush but he has not explicitly made use of it in setting up the rate expression for the simplified reaction that he considered, the association of two atoms to form a diatomic molecule. A more direct application of this fundamental principle turns out to be of interest, not only in connection with the example which Rodebush has treated, but also because it enables one to extend the method and apply it to the bimolecular association of polyatomic molecules, which is of more practical importance, since we may assume that the excess energy may always be taken care of by transfer to the internal vibrations, whereas the bimolecular association of two atoms is a very improbable process, as the presence of a third body is required to remove the excess energy.[3]

Only four bimolecular associations have been studied experimentally in sufficient detail for our purposes: the hydrogenation of ethylene,[4a] and the polymerizations of ethylene,[4b] butadiene,[5a] and isoprene.[5b] One of the characteristic features of these associations is the occurrence of a so-called steric factor which gives the fraction of the total number of collisions (calculated from kinetic theory) that leads to reaction. Except in the case of the hydrogenation of ethylene these steric factors are quite small. A complete theory of bimolecular association would account for these steric factors. Their actual calculation, however, would involve assumptions as to the mechanism of reaction, which in our present state of knowledge would necessarily be highly speculative. In the following, therefore, we have adopted a less ambitious program and have been content to put forth an interpretation of the experimental results, except in the case of the hydrogenation of ethylene for which we have proposed a mechanism and calculated the absolute rate.

[1] Rodebush, J. Chem. Phys. **1**, 440 (1933).

[2] See Tolman, *Statistical Mechanics*, pp. 302, 306, Chem. Cat. Co., 1927.

[3] See Kassel, *Kinetics of Homogeneous Gas Reactions*, pp. 38, ff., Chem. Cat. Co., 1932.

[4] Pease, J. Am. Chem. Soc. (a) **54**, 1876 (1932), (b) **53**, 613 (1931). Pease's conclusions regarding the ethylene polymerization have been questioned by Storch, J. Am. Chem. Soc. **56**, 374 (1934), who, however, worked in a different pressure range.

[5] Vaughan, J. Am. Chem. Soc. (a) **54**, 3863 (1932), (b) **55**, 4109 (1933).

General Considerations

In order to get the expression in the best form for our purposes, and in order that there may be no misunderstanding as to the meaning of the various terms involved, we shall consider the derivation from first principles of the equilibrium constant for a reaction of the type $M_2+M_3\rightarrow M_1$ where M_1, M_2 and M_3 are, in general, polyatomic molecules.

We assume that our system is enclosed in a constant volume V, is kept at a temperature T, that the number of molecules M_1 is N_1, and that the numbers of *uncombined* M_2 and M_3 are, respectively, N_2 and N_3. We define the entropies per molecule, S_1, S_2 and S_3, by expressions of the type[6] $S_1=k\ln(W_1/h^{n_1})$, where k is the Boltzmann constant and h Planck's constant, n_1 is the number of degrees of freedom of the molecule M_1, and

$$W_1=\int_0^\infty (d\omega_1/d\epsilon_1)\exp\left[-(\epsilon_1-\bar{\epsilon}_1)/kT\right]d\epsilon_1. \quad \text{(A)}$$

Here $(d\omega_1/d\epsilon_1)d\epsilon_1$ is the volume in the phase space of a single molecule which lies between energies ϵ_1 and $\epsilon_1+d\epsilon_1$ and $\bar{\epsilon}_1$ is the average energy per molecule. $h^{-n_1}\int_0^\infty(d\omega_1/d\epsilon_1)\exp(-\epsilon_1/kT)d\epsilon_1$ is the *Zustandsumme* or partition function of the molecule; we assume that we are at such a high temperature that the summation can be replaced by an integral. $(d\omega_1/d\epsilon_1)d\epsilon_1$, the total volume of its phase space which the molecule can visit if its energy be between ϵ_1 and $\epsilon_1+d\epsilon_1$, is multiplied by the relative probability that it be in this energy range as compared to the probability that it be in an equal range near $\bar{\epsilon}_1$. W_1 may therefore be said in a certain sense to be the total effective volume in the phase space of the molecule M_1 which conforms to the condition that its temperature be T (corresponding to $\bar{\epsilon}_1$).

The total entropies for each of the various types of gas which exist in the system are, then, N_1S_1, N_2S_2 and N_3S_3. But these expressions assume that specified individuals of the type M_2 and M_3 are uncombined and other specified individuals are combined. In setting up an expression for the whole system we must allow for the interchange of molecules, in particular for the interchange of *combined* M_2 and M_3 with each other and with uncombined ones.[7] In this way we get an expression for the entropy of the whole system

$$S=N_1S_1+N_2S_2+N_3S_3+k\ln\left[(N_1+N_2)!(N_1+N_3)!/N_1!N_2!N_3!\right].$$

If we allow N_1, N_2 and N_3 to vary

$$\delta S=S_1\delta N_1+S_2\delta N_2+S_3\delta N_3+(\delta N_1+\delta N_2)k\times\ln(N_1+N_2)+(\delta N_1+\delta N_3)k\ln(N_1+N_3)-\delta N_1k\ln N_1-\delta N_2k\ln N_2-\delta N_3k\ln N_3.$$

However, on account of the conservation of particles, we have $\delta N_1=-\delta N_2=-\delta N_3$. So

$$\delta S=\delta N_1(S_1-S_2-S_3)-\delta N_1k\ln(N_1/N_2N_3)=\delta N_1[\Delta S-k\ln(N_1/N_2N_3)].$$

Now if ΔE is the change of energy on association then the entropy change of the thermostat is $-\delta N_1\Delta E/T$. At equilibrium we must have $\delta S-\delta N_1\Delta E/T=0$, which gives

$$k\ln(N_1/N_2N_3)=\Delta S-\Delta E/T.$$

Now the equilibrium constant is equal to VN_1/N_2N_3. It is also equal to k_2/k_1, where k_1 and k_2 are the rate constants of the unimolecular decomposition and bimolecular association, respectively. Hence

[6] Our definition of the entropy per molecule is just the usual one; it may be shown to be entirely equivalent to the upper limit of Eq. (208), p. 109 of Tolman.[2] (Including the lower limit of Tolman's equation is equivalent to subtracting off the part of the entropy due to any multiplicity of the lowest state, which we, of course, do not wish to do. Tolman's equation is given for rotational entropy only, but may be readily generalized.) On the other hand, our definition of the total entropy differs from that ordinarily used in thermodynamics. The relation between them is given by S_1 (thermo) $=S_1$ (ours) $-\ln N_1!$

[7] In thus assuming that we can distinguish between individual molecules of the same kind, we are of course using the Boltzmann statistics rather than the Fermi or Bose statistics. It is, however, well known that the latter types of statistics will give the same results at high temperatures as the Boltzmann. The fact that molecules of the same kind are really indistinguishable simply reduces the entropy, S, of the whole system by $k\ln[(N_1+N_2)!(N_1+N_3)!]$, $(N_1+N_2)!$ and $(N_1+N_3)!$ being the number of permutations of all (combined and uncombined) M_2 and M_3, respectively. At high temperatures, where the energy levels are very close together compared with the total energy, this amounts simply to a thinning out of the number of possible energy levels, which can make no difference in the distribution function, nor in any of the observable properties of the system. Our calculations come to rest ultimately upon the entropy expression for the case, $N_1+N_2=N_1+N_3=1$. At high temperatures the value of this expression will obviously be independent of whether Boltzmann, Fermi, or Bose statistics are used.

$$k \ln (k_2/k_1) = \Delta S + k \ln V - \Delta E/T.$$

If now we let our volume be unity, and define our standard entropy as that for unit volume, we may write

$$\ln (k_2/k_1) = \Delta S^\circ/k - \Delta E/kT. \quad (1)$$

This has nearly the same form as the ordinary thermodynamic equation, but it must be noted that entropy, as we have defined it, has slightly different properties than the thermodynamic entropy.[6] Our entropy doubles when the amount of gas doubles, the volume remaining the same. The thermodynamic entropy doubles when the amount of gas is doubled if the *pressure* remains the same. Also our ΔS refers to a process taking place at constant volume while the ordinary thermodynamic ΔS assumes that all the partial pressures remain fixed, which accounts for the slight difference in form between our equation and the usual thermodynamic one used by Rodebush.

In order to determine the absolute values of k_1 and k_2 we must be able to separate the right-hand side of Eq. (1) into two parts. The first term can be so divided by the relation[8]

$$-\Delta E = \epsilon_a - \epsilon_a', \quad (2)$$

where ϵ_a and ϵ_a' are, respectively, the activation energies of the unimolecular decomposition and the bimolecular association. We may then write

$$k_1 = A_1 \exp(-\epsilon_a/kT); k_2 = A_2 \exp(-\epsilon_a'/kT), \quad (3)$$

where the A's could be determined if we could divide the ΔS° term in a similar unique fashion.

Before considering how to do this, however, it will be well to examine the general formula for the entropy of a polyatomic molecule.[9] The standard entropy S_i° (where $i = 1, 2$, or 3) may be conveniently expressed in the following form

$$S_i^\circ = k \ln B_i + k \ln C_i + k \ln D_i + k \ln E_i, \quad (4)$$

where $\ln B_i$ is the part due to the translational motion of the molecule (that is to say, $B_i = W_{it}/h^{n_{it}}$, where $n_{it} = 3$ is the number of translational degrees of freedom and W_{it} is the total volume in the translational part of the phase space of the molecule, which conforms to the condition that the gas is at temperature T), $\ln C_i$ is the part due to rotation, $\ln E_i$ the part due to vibration, and $D_i = \rho_{ie}\rho_{in}$, where ρ_{ie} is the degeneracy due to electronic spin and ρ_{in} that due to nuclear spin.

We may calculate B_i, C_i, and E_i by means of relations which (neglecting a power of h) are of exactly the same form as Eq. (A), except that each one deals with its specific part, the translational, the rotational, or the vibrational part, of the energy and phase space, this being, in fact, the usual method for calculating these entropies.[10] General formulas may be given[11] for B_i and E_i.

$$B_i = (2\pi e m_i kT/h^2)^{\frac{3}{2}} \quad (5)$$

where e is the base of the natural logarithms, and m_i is the mass of the molecule.

$$\ln E_i = \sum_j \{(h\nu_{ij}/kT)[\exp(h\nu_{ij}/kT) - 1]^{-1} - \ln[1 - \exp(-h\nu_{ij}/kT)]\}, \quad (6)$$

where the ν_{ij} are the frequencies of the molecule, the summation being taken over all frequencies. In each specific instance it will be necessary to consider the rotational terms separately. However, we shall often find it convenient to divide the term C into parts, writing

$$C = C_i' C_i'' C_i''' \cdots, \quad (7a)$$

where

$$C_i' = \pi^{-1}(8\pi^3 e I_i' kT/h^2\sigma_i'^2)^{l_i'/2},$$
$$C_i'' = (8\pi^3 e I_i'' kT/h^2\sigma_i''^2)^{l_i''/2}, \quad (7b)$$
$$C_i''' = (8\pi^3 e I_i''' kT/h^2\sigma_i'''^2)^{l_i'''/2}.$$

In these equations I_i' or I_i'' or I_i''' or $\cdots$ represents the moment of inertia connected with a given degree or group of degrees of freedom of rotation and $I_i' > I_i'' > I_i''' > \cdots$; $l_i' + l_i'' + l_i''' + \cdots$ gives the total number of degrees of freedom of rotation; and σ_i', σ_i'', σ_i''', $\cdots$ are the symmetry numbers related to the respective rotations.

---

[8] Gershinowitz and O. K. Rice, J. Chem. Phys. **2**, 275 (1934).

[9] This has been discussed by Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933).

[9] See Tolman, reference 2, p. 109.

[11] If V were not unity we would have, instead, $B_i = (2\pi e m_i kT/h^2)^{\frac{3}{2}} V$. Thus for the entropy of the N_i molecules we would have $kN_i \ln[(2\pi e m_i kT/h^2)^{\frac{3}{2}} V]$. If now to this expression we should add the term $-k \ln N_i! \cong -kN_i \ln N_i + kN_i \ln e = -kN_i (\ln N_i - 1)$, in order to get the thermodynamic entropy (see reference 6) we would arrive at the familiar Sackur-Tetrode expression. (See Tolman, reference 2, p. 138.)

Let us now return to the question of determining A_1 and A_2 separately. If we assume as a zero approximation that A_1 does not depend upon the properties of M_2 and M_3 and A_2 does not depend upon the properties of M_1, and write, provisionally,[12]

$$A_1 \doteq (B_1C_1D_1E_1)^{-1}kT/h \tag{8a}$$

and

$$A_2 \doteq (B_2C_2D_2E_2B_3C_3D_3E_3)^{-1}kT/h \tag{8b}$$

we see from Eqs. (3) and (4) that these expressions are consistent with Eq. (1). The significance of (8a) and (8b) becomes evident if we note that $B_1C_1D_1E_1$ is just equal to the phase-space, divided by h^{n_1}, of a single molecule M_1 confined in unit volume, while $B_2C_2D_2E_2B_3C_3D_3E_3$ is that of a single pair of molecules M_2 and M_3 confined in unit volume. They give the probability that the system be in a region of the phase space equivalent to one *single* quantum state, divided by the characteristic time, h/kT. To say that the rates are given by the above expressions is essentially equivalent to stating that there is only *one* energy distribution which will lead to reaction, and that the average time necessary for reaction to occur from this distribution is h/kT. These provisional values of A_1 and A_2 will be very small; but if these expressions could be modified in the proper manner, one could determine the rate of reaction. The first correction will have to do with the time factor; this is included in the discussion of the collision factor, in the next section. The other necessary modifications could be made, if one could determine in what states the molecules actually exist when reaction occurs.

One such modification is easily made, and serves to illustrate a principle of which we shall make much use. In general we do not expect the probability of reaction to be affected by the spin degeneracy of the nuclear and electronic states, provided, as we shall assume for the cases of interest to us here, the spin degenercy does not change when the reaction takes place.[13] In other words the number of such states available for the reaction is the same as the total number of such states. Therefore we multiply A_2 by the corresponding entropy expression D_2D_3. A_1 must, of course, be multiplied by the same thing in order that Eq. (1) may continue to be valid. But by the assumptions we have made $D_1 = D_2D_3$ and these three quantities are simply eliminated from the rate expressions leaving,

$$A_1 \doteq (B_1C_1E_1)^{-1}kT/h, \tag{9a}$$

$$A_2 \doteq (B_2C_2E_2B_3C_3E_3)^{-1}kT/h. \tag{9b}$$

We would, of course, have arrived at the same result if we had considered A_1 first and noted that both expressions have to be multiplied by D_1.

The Collision Factor

We shall next obtain the collision factor, which we define as the number of collisions per cc per second at unit concentration (one molecule per cc). This quantity, which must be an important part of A_2, we shall get by a method which we believe brings out the physical principle involved more clearly than that of Rodebush.

When a diatomic molecule splits into two atoms it is easy to trace the fate of each degree of freedom. The two rotational and one vibrational degrees of freedom simply pass over into three of translation. To establish a similar correspondence for the dissociation of a polyatomic molecule is more difficult. In general a polyatomic molecule has three rotational degrees of freedom (neglecting internal rotation), and after dissociation *each* fragment has three degrees of freedom of rotation and three degrees of freedom of translation. Since the total number of degrees of freedom in the system must be conserved these six new degrees of freedom must have been vibrations in the associated molecule. The chief difficulty is encountered in determining which of the original degrees of freedom corresponds to a particular new one, and of course no exact answer is possible on account of the change in character of the normal vibrations. However, it will usually be reasonable to assume that the two rotational degrees of freedom connected with the largest moments of inertia of M_1 (which moments we assume, for the sake of simplicity,

[12] We use the symbol $\doteq$ to mean "equals provisionally."

[13] The reaction $H_2 \rightarrow 2H$ is a reaction in which the net spin degeneracy *does* change, and in which our considerations will not hold. The effect of spin on the steric factor has been considered generally by Bates and Rosen (unpublished work).

to be equal, as in the symmetrical top), together with one degree of freedom which is concerned with the relative vibration of the parts[14] which are to form M_1, are connected with the relative translational motion of M_2 and M_3. We may thus break (9a) and (9b) each into two factors,

$$A_1' \doteq (B_1C_1'E_1')^{-1}kT/h, \qquad (10a)$$

$$A_2' \doteq (B_2B_3)^{-1}kT/h, \qquad (10b)$$

in which the degrees of freedom just mentioned and those concerned with the translation of the center of gravity of the system are included; and

$$A_1'' \doteq (C_1''E_1'')^{-1}, \qquad (11a)$$

$$A_2'' \doteq (C_2E_2C_3E_3)^{-1}, \qquad (11b)$$

which include all the rest of the degrees of freedom. We now make the assumption that A_1' and A_1'', A_2' and A_2'' are independent and can be treated separately.

We shall now apply to these equations the method that was used in the preceding section to eliminate D_1, D_2 and D_3 from Eqs. (8a) and (8b). Let us first consider the unimolecular reaction. In theories of unimolecular reactions it is usually assumed that the probability of dissociation is independent of the rotational and translational energy of the molecule. This means that all rotational and translational states are available for reaction. Therefore A_1' should be multiplied by B_1C_1'. A_2' must be multiplied by the same factors as A_1'. We thus get

$$A_1' \doteq (E_1')^{-1}kT/h,$$

$$A_2' \doteq (B_1C_1'/B_2B_3)kT/h.$$

It can easily be seen that if the expression for A_2' be multiplied by $e\exp(-Q-kT/2)/kT$ it gives the number of collisions per unit time with energy along the line of centers greater than Q, provided that the effective radius of the collision is given by r_1', the distance which come into[15] I_1'. $Q+kT/2$ is the part of the activation energy connected with the translational motion, since the average energy of all pairs of molecules in collision exceeds the average energy of all pairs by[16] $kT/2$. The factor, e, that it has been necessary to introduce is not included in the activation energy and hence it must also be multiplied into A_1', giving the final expressions

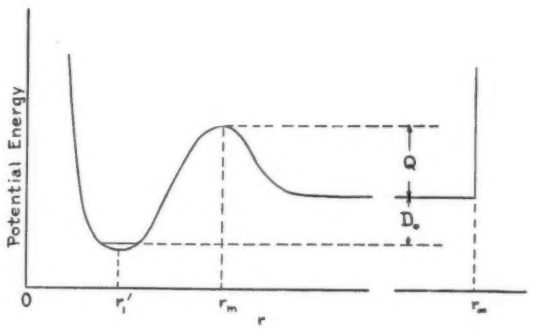


FIG. 1.

$$A_1' = e(E_1')^{-1}kT/h, \qquad (12a)$$

$$A_2' = e(B_1C_1'/B_2B_3)kT/h. \qquad (12b)$$

Effectively, this imposes a condition on the vibration involved in E_1', which also includes any correction which may be necessary in the time factor h/kT. The nature of the condition thus imposed we shall now proceed to investigate.

Suppose the potential between M_2 and M_3 (assuming for simplicity that it is a function of r alone) is of the form[17] shown in Fig. 1. The potential is supposed to go to infinity at r_∞, which ties the two molecules together, and which converts the continuous part of the spectrum into a close spaced set of discrete levels. We assume throughout that $r_\infty \gg r_m$. We can now consider the distribution of energy in this system of two molecules. We let K be the asymptotic value of the relative kinetic energy of a pair of molecules in the continuum.[18] The number of energy levels lying between K and $K+dK$ will be given by[19] $r_\infty(2\mu/Kh^2)^{\frac{1}{2}}dK$, where μ is the reduced mass of M_2 and M_3. The probability of finding a pair of molecules in an energy level

[14] This vibration actually will not be a normal vibration, but we make the approximation of treating it as such. The considerations of this section can at best have only an approximate significance.

[15] Tolman, reference 2, p. 70.

[16] See Gershinowitz and Rice, reference 8, p. 275 (footnote 11).

[17] As far as the considerations of this paragraph go, the hump at r_m may be vanishingly small.

[18] We neglect the possibility of leakage through the hump, and assume always that K is greater than Q.

[19] This is the usual expression, obtained from the boundary conditions which are imposed on the wave functions.

of kinetic energy K is given by the usual expression,

$$\exp\left[-(D_0+K)/kT\right]/\sum_i \exp\left(-\varepsilon_i/kT\right),$$

where D_0 is the dissociation energy from the lowest vibrational level, and the summation is taken over all possible energy levels[20] ε_i. Now if a pair of molecules has a relative kinetic energy K the relative velocity is $(2K/\mu)^{\frac{1}{2}}$, and a time equal to $2r_\infty(2K/\mu)^{-\frac{1}{2}}$ will be required for r to go from its smallest possible value to r_∞, and back again. Thus, on the average, the number η of times per unit time that a given pair of particles having relative kinetic energy greater than Q will pass a given value of the coordinate, r, while moving so that r is increasing, will be

$$\eta=\int_Q^\infty 2^{-1}r_\infty^{-1}(2K/\mu)^{\frac{1}{2}}r_\infty(2\mu/Kh^2)^{\frac{1}{2}}$$
$$\times\exp\left[-(D_0+K)/kT\right]dK/\sum_i \exp\left(-\varepsilon_i/kT\right)=$$
$$(kT/h)\exp\left[-(D_0+Q)/kT\right]/\sum_i\exp\left(-\varepsilon_i/kT\right).$$

Now we can evaluate approximately the sum in the denominator (which is the *Zustandsumme*) on the assumption that when the molecules M_2 and M_3 are bound together they behave as a simple harmonic oscillator with frequency ν_1'. We have

$$\sum_i \exp\left(-\varepsilon_i/kT\right)=\left[1-\exp\left(-h\nu_1'/kT\right)\right]^{-1}$$
$$=E_1'\exp\left(-\varepsilon_{av}/kT\right),$$

where ε_{av} is the average energy of oscillation. This last relation will be understood by reference to Eq. (6) if we remember that the average energy of the oscillator is given by $h\nu_1'[\exp(h\nu_1'/kT)-1]^{-1}$. Therefore

$$\eta=(kT/h)e(E_1')^{-1}\exp\left[-(D_0+Q-\varepsilon_{av}+kT)/kT\right].$$

Since, as may be readily verified, D_0+Q+kT is the average energy of the pairs of molecules whose coordinates, r, pass a given value, $D_0+Q-\varepsilon_{av}+kT$ is the activation energy, provided η may be assumed to give the rate of dissociation of the complex M_1. The part of the expression in front of the exponential is just equal to the right-hand side of (12a). It is thus seen that the condition, which we have above imposed on the vibration, is just that it be allowable to assume that η gives the rate of decomposition of M_1, or, in other words, that it is possible to calculate the rate of decomposition from the flux at equilibrium.

That the effective collision radius is equal to r_1' depends, as we have noted, on the assumption that the probability of decomposition is independent of the rotational state. Actually, of course, this is not strictly true, and the calculated value of the collision radius will be correspondingly altered. A simple calculation, in which we make the simplifying assumption that the combined pair of molecules M_2 and M_3 acts like a simple diatomic molecule, will illustrate how this comes about. If the molecule, M_1, is in a rotational state defined by the quantum number j, it is well known that this results in what is effectively an added term to the potential energy, equal to $\kappa^2j(j+1)/r^2$, where $\kappa^2=8\pi^2\mu/h^2$. Thus the minimum at r_1' is reduced by approximately $\kappa^2j(j+1)/(r_1')^2$, so that the dissociation energy becomes $D_0-\kappa^2j(j+1)/(r_1')^2$. Similarly Q becomes $Q+\kappa^2j(j+1)/r_m^2$. Thus, replacing Q and D_0 in the expression for η by these new quantities, we get the following relation between η_j and η_0 (where the subscript indicates the rotational state):

$$\eta_j=\eta_0\exp\left[\kappa^2j(j+1)\{(r_1')^{-2}-r_m^{-2}\}/kT\right].$$

Now the probability that the rotational state should be the jth is given approximately by

$$P_j(r_1')/\sum_{j=0}^{j=\infty}P_j(r_1'),$$

where

$$P_j(r_1')=(2j+1)\exp\left[-\kappa^2j(j+1)(r_1')^{-2}/kT\right].$$

The average probability of decomposition from any state will be given by

$$\sum_{j=0}^{j=\infty}\eta_jP_j(r_1')/\sum_{j=0}^{j=\infty}P_j(r_1')=\eta_0\sum_{j=0}^{j=\infty}P_j(r_m)/\sum_{j=0}^{j=\infty}P_j(r_1').$$

As may readily be seen by evaluating the sums in the usual manner, this becomes equal to $\eta_0r_m^2(r_1')^{-2}$ at high temperatures. To get a more exact expression for A_1' than is given by Eq. (12a) it is thus necessary to multiply the right-hand side of (12a) by $r_m^2(r_1')^{-2}$. Naturally the

[20] This includes the continuous energy levels, but we can assume that they make but a negligible contribution to the sum.

right-hand side of (12b) must be multiplied through by the same quantity, and it is obvious that the collision radius r_1' is thus replaced by r_m, which is certainly a very reasonable result. Since, however, r_m will not ordinarily be expected to differ greatly from r_1', it will generally be safe to use the latter as an approximation.

The Steric Factor

The steric factor is to be obtained by a consideration of (11b). To take care of the factors E_2 and E_3, we shall assume either (1) that the probability that M_2 and M_3 will recombine does not depend on their vibrational state, that is, that the activation energy is entirely translational energy or (2) that a certain localization of energy in some particular bond or bonds of either M_2 or M_3 or both is necessary, but that the entropy of those states which can react is the same as the entropy of all states.[21] This is essentially similar to the assumptions of Kassel's theory of unimolecular decompositions,[22] and our recent work[8] makes it appear very probable that this assumption is approximately correct, especially if the localization of energy does not affect the frequencies of the molecule. Thus we multiply A_2'' through by E_2E_3.

There seem, however, to be grounds for the belief that not all rotational states[23] of M_2 and M_3 are equally available for association. (Do not confuse with the statement of the last section that all rotational states of M_1 are equally available for dissociation.) A comparison of the experimental data with the numerical values of the entropy shows that the steric factors are of the order of magnitude that would be expected if some of the rotational degrees of freedom are more or less "frozen out" when reaction occurs. That is, in order that reaction may take place there must be a certain orientation of the molecules with respect to each other. Therefore, instead of multiplying (11b) by C_2C_3 we can multiply through only by some of the primed factors of these quantities, i.e., those representing rotations that have no effect on the probability of association. The factors that remain in the denominator then give us the steric factor.[24] If there were some way of determining which rotational degrees of freedom are relevant to each reaction we could calculate an absolute rate for the reaction that could be compared with experiment. There are, however, so little data on the mechanism and kinetics of these reactions, that rather than adopt particular mechanisms we have preferred to develop, on the basis of the above considerations regarding the degrees of freedom involved in the reaction, a new method of handling the experimental data.

First we set up a collision factor as in Eq. (12). We then divide the experimental absolute rate by this collision factor to get what we may call an experimental A_2''. Next we set up an expression of the form $[\pi^{-\frac{1}{2}}(8\pi^3eIkT/h^2)]^{-n/2}$, in which we have neglected the symmetry factors. For I we use the geometric mean of the estimated moments of inertia of the associating molecules. The factor of $\pi^{-\frac{1}{2}}$ is introduced as a compromise, since we do not know which degrees of freedom are frozen out and cannot tell whether they should have the factor of π^{-1} such as appears in C_i' of Eq. (7b). We can then determine n so the expression will best reproduce the experimental value of A_2''. This value of n will tell us approximately how many degrees of freedom of rotation must be fixed, or, in other words, how stringent are the conditions that must be satisfied in order that reaction may take place when the

[21] The reasonableness of this assumption is evident from the following considerations. If we consider a simple harmonic oscillator molecule and arbitrarily say that every molecule whose vibrational energy is greater than a certain amount shall be considered one of a new species, then the vibrational entropy calculated for this new species is the same as that for all the molecules. Localization of the vibrational energy of the molecule is very much like the excitation of a single mode of vibrations, provided the frequencies of the molecule are not changed in the process.

[22] Kassel, J. Phys. Chem. **32**, 1065 (1928).

[23] It is understood when we speak of a "rotational state" in this manner that it should not be thought of as too closely associated with the ordinary rotational levels of the molecule. We really use the term "rotational state" as a shorthand expression for a region in the phase space which has a certain definite size, namely h or some power thereof, according to the number of dimensions involved.

[24] It is possible that, for reaction to occur, the molecule must be more or less twisted out of shape and that something equivalent to the fixing of one or more vibrational degrees of freedom is also necessary. As already noted, we have neglected this entirely. In general the restriction of a vibrational degree of freedom would have much less effect on the magnitude of the steric factor than the fixing of a rotation since the terms in the summation of Eq. (6) are relatively small for the frequencies that ordinarily occur.

TABLE I.

Reaction	A_2 (expt)	I_1' (est)[a]	I (est)[a]	A_2'[b]	A_2''	n
Ethylene and Ethylene[4b]	6.6×10^{-13}	1.5×10^{-38}	0.3×10^{-38}[c]	1.72×10^{-10}	3.8×10^{-3}	1.7
Isoprene and Isoprene[5b]	1.4×10^{-12}	4×10^{-38}	1.1×10^{-38}	2.25×10^{-10}	6.2×10^{-3}	1.1
Butadiene and Butadiene[5a]	6.8×10^{-14}	2.7×10^{-38}	0.6×10^{-38}	2.18×10^{-10}	3.1×10^{-4}	1.9

(a) These are for the most part rough estimates made with the aid of the structural formulas of the compounds involved, insofar as these are known, and the figures of Badger, Phys. Rev. **45**, 648 (1934).

(b) Except in the case of ethylene the expression for A_2' in Eq. (12b) has been used as it stands and has not been divided by 2, for although the two molecules colliding are the same it is unlikely that they form a symmetrical configuration on combining. See Rodebush, reference 1, pp. 441, 443.

(c) Average includes large moments only. In this case, allowance has been made for the symmetry factor and π^{-1} has been put in place of $\pi^{-\frac{1}{2}}$ in the expression for calculating n.

molecules collide. n should, of course, always be a small number.

We have applied this procedure to the various association reactions that are known (excepting the hydrogenation of ethylene which will be further considered below), and the results are presented in Table I.

The value of n for isoprene is surprisingly low, since it is the most complicated molecule and we might expect that it would have the most stringent conditions with respect to orientation. The relative values of the n's in the table, however, agree with the relative magnitudes of the steric factors calculated by Vaughan,[5] using kinetic theory collision numbers. We would expect that both molecules would have to be oriented thus fixing at least one degree of freedom for each. If we arbitrarily set $n=2$ for isoprene, we miss the observed rate by a factor of about 50, which could be interpreted to mean that each degree of freedom would be only partly frozen out, so that there would be 7 ($\cong\sqrt{50}$) quantum states in which reaction could occur. If the polymerization of isoprene results in the creation in the polymer of two very low vibrational frequencies, corresponding to the two degrees of freedom which are fixed, then this would not be unexpected, for in the reverse reaction decomposition could occur from a number of levels, corresponding to the number of low energy states excited. The other rotations of the isoprene, which do not have to be fixed, become internal rotations in the molecule, which are completely excited, at least in the excited state of the polymer which is first formed and which conversely, is the state from which decomposition takes place.

In the case of butadiene, where n is about 2, the evidence seems to indicate that a dicyclic, and, hence, rather stiff structure is formed, and the structure of the polymer seems to be not too closely related to the structure of the butadiene. Thus one might expect that more rotations would have to be fixed, and so it may very well be that actually a greater number, perhaps 3 or 4 degrees of freedom are *partially* frozen out.

The cases discussed illustrate what can be done with the approach to the experimental data developed above. We believe that this method gives a greater insight into the actual mechanism of the reaction than a mere calculation of collision frequency and steric factor by means of kinetic theory collision diameters.

THE COMBINATION OF ETHYLENE AND HYDROGEN[25]

This reaction needs special treatment, since the relation between the degrees of freedom before and after combination is more complicated than assumed above. Ethane has 3 translational degrees of freedom, 4 rotational (one due to the free rotation of the methyl group), and 17 vibrational. The hydrogen and ethylene between them have 6 translational degrees of freedom, 5 rotational, and 13 vibrational. It is obvious that 3 of the rotational degrees of freedom of the ethane correspond directly to the 3 rotational degrees of freedom of ethylene, while the degree of freedom corresponding to

[25] We assume in this discussion that the hydrogen molecule comes off in one step from the ethane, and that no chain, such as suggested by F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934) is involved. If there is such a chain, then, of course, all the separate steps in the chain will need separate treatment.

the free rotation of the methyl groups presumably goes over into a transverse vibration of the ethylene. Thus, in the unimolecular reaction we must have 6 vibrational degrees of freedom of the ethane going over into 3 of relative translation, 2 of rotation of the hydrogen, and 1 of vibration of the hydrogen. We thus separate off these degrees of freedom, together with the rest of the translation and write:

$$A_1' \doteq (B_1E_1')^{-1}kT/h, \tag{13a}$$

$$A_2' \doteq (B_2B_3C_3E_3)^{-1}kT/h, \tag{13b}$$

where subscripts 1, 2 and 3 refer to ethane, ethylene, and hydrogen respectively, E_1' being the term for the 6 vibrations of the ethane which are concerned.

Now if we can assume that the vibration and rotations of the ethylene have no effect on the reaction, then the proper evaluation of A_2' will actually give us A_2 and so the rate of recombination of ethylene and hydrogen.

The vibrations of ethane included in E_1' may be thought of as belonging to the two hydrogens which are going to leave the ethane, though this can only be approximate, as such vibrations would not be normal vibrations. It is obvious that before the reaction occurs the forces holding these hydrogen to the rest of the structure will have become very much weakened. Thus we will not be able to take care of them simply by multiplying A_1' through by E_1'. Rather we should think of some intermediate complex, in which these two hydrogens have to all intents and purposes already formed a hydrogen molecule, with its characteristic rotations and vibrations; this hydrogen molecule is, however, still held to the ethylene by weak forces. The hydrogen molecule would vibrate with respect to the ethylene, and could rotate freely around the ethylene, at least about the line of centers of the carbon atoms. The hydrogen molecule would be expected to be about 1A from the line of centers of the carbon atoms and the effective moment of inertia will be obtained approximately by multiplying the mass of a hydrogen molecule by the square of this distance, and is thus 3.3×10^{-40} c.g.s. units. Motion along the line of centers will probably be more of a vibration than a rotation, but it seems reasonable to assume in calculating the entropy that it is actually more like a rotation with about the same moment of inertia as that given above. Assuming now that all of these "rotational states" are equally available for reaction, that to take care of the vibration of the hydrogen molecule with respect to the ethylene we multiply by e, as above, and that the various vibrational and rotational states of the hydrogen molecule are all equally good for reaction, it is seen that we should multiply A_1' and hence A_2' by $eB_1C_0C_3E_3$, where

$$C_0 = 8\pi^2 eI_0kT/h^2, \tag{14}$$

I_0 being 3.3×10^{-40} c.g.s. units. This gives us, at 800°K,

$$k_2 = (eB_1C_0/B_2B_3)(kT/h)\exp(-\epsilon_a'/kT)$$

$$= 1.66\times10^{-10}\exp(-\epsilon_a'/kT). \tag{15}$$

The experimental value[26] is $0.91\times10^{-10}\exp(-\epsilon_a'/kT)$. ($\epsilon_a'$ has the value 44,750 calories per mole.)[27] There is, therefore, very close agreement between experiment and theory, on the basis of the assumptions we have made. Had the experimental value come out much smaller than the theoretical, we would have presumed that our assumption that the vibration of the hydrogen molecule in the intermediate complex along the line of centers of the carbon atoms was more restricted than we supposed, and this would have corresponded to a restriction in the direction in which the hydrogen molecule could leave the ethylene. Any such restriction is certainly far less than would correspond to the freezing out of one rotational degree of freedom. This last observation affords us an insight into the relative importance of the various degrees of freedom with respect to probability of reaction.

While in the above we have restricted ourselves to a discussion of bimolecular associations, we have incidentally obtained an equal amount of information about the reverse reactions. In future work we shall attempt to discuss some of the experimentally known unimolecular reactions from this point of view.

---

[26] We have recalculated this value from the original data of Pease,[4a] since he has made several minor errors in the calculation of his results. Our effective collision diameter is appreciably different from what he assumes.

[27] Gershinowitz and Rice, reference 8, p. 276.

The Theory of the Glass Electrode. III

Statistical Explanation of the Alkaline Solution Behavior*

MALCOLM DOLE, *Department of Chemistry, Northwestern University*

(Received July 11, 1934)

The application of Gurney's quantum and statistical mechanical theory of electrochemistry to the glass electrode results in an equation for the alkaline solution behavior identical with one previously obtained by the author except that the constants of the equation have a more reasonable significance. A qualitative explanation of the inability of negative ions to affect the glass electrode potentials is also given.

THE behavior of the glass electrode in alkaline solutions has been interpreted in a number of different ways by Hughes, Horovitz, Lengyel, Michaelis, Quittner, MacInnes and Belcher, Gross and Halpern and the author,[1] but as yet no physically satisfactory picture of the glass electrode has been presented. The first quantitative treatment of the glass electrode was that of the author[2] who applied liquid junction theory equations to the glass electrode and obtained the following equation

$$\Delta E=\frac{RT}{F}\ln\left\{\frac{(u_{Na}/u_H)c_{Na}+c_H}{c_H}\right\}, \qquad (1)$$

where ΔE is the error of the glass electrode, u_{Na}, u_H, c_{Na} and c_H the mobilities and concentrations of the sodium and hydrogen ions, respectively. Eq. (1) agreed with the data provided a suitable choice of the constants u_{Na} and u_H was made; but the assumptions made in the derivation of Eq. (1) namely, that the hydrogen ion has a mobility 10^{11} times that of any other ion and that negative ions have zero mobility in the liquid junction could not be defended in any reasonable way on the basis of liquid junction theory. Statistical mechanics, however, seems to offer a more satisfactory explanation of the glass electrode behavior. Gurney[3] has developed a quantum and statistical mechanical theory of electrochemistry which gives a new viewpoint with which to picture electrode mechanisms. This theory, which will not be described here, has been applied by Gurney to resolve the Volta potential difference controversy, to derive equations for interface and electrode potentials, to explain overvoltage and in some unpublished work to describe the plating out of alloys. Since the plating out of alloys consists in the deposition of two kinds of ions, Gurney's mathematical treatment for alloys is particularly applicable to the glass electrode where we have in alkaline solutions two kinds of ions affecting the observed e.m.f. The following theoretical treatment of the glass electrode is based on Gurney's mathematical theory of the plating out of alloys. Because the two mathematical treatments are similar, one must not infer that we conceive glasses to be similar physically to alloys. In alloys the positive ions maintain fixed positions while the negatively charged electrons are mobile and carry the electrical current. In glasses on the contrary, it is the negative silicate ions that are fixed, the electrical conduction being due to the positive ions. To apply Gurney's theory to the glass electrode it is only necessary to assume that the positive ions in the glass occupy positions of equilibrium and that the distribution of ions in the different energy levels of these equilibrium positions follows the Boltzmann distribution law.

* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Chicago, September, 1933.

[1] See the author's first paper, J. Am. Chem. Soc. **53**, 4260 (1931) for bibliography up to 1931. More recent papers are Buchböck, Zeits. f. physik. Chemie **A156**, 232 (1931); MacInnes and Belcher, J. Am. Chem. Soc. **53**, 3315 (1931); S. I. Ssokolov and A. H. Passynsky, Zeits. f. physik. Chemie **A160**, 366 (1932); M. Dole, J. Am. Chem. Soc. **54**, 3095 (1932); P. Gross and O. Halpern, J. Chem. Phys. **2**, 136 (1934).

[2] M. Dole, J. Am. Chem. Soc. **53**, 4260 (1931).

[3] R. W. Gurney, Proc. Roy. Soc. **A136**, 378 (1932); **A134**, 137 (1931).

Application of Gurney's Theory to the Glass Electrode

The hydrogen electrode function of glass may be explained according to statistical mechanics by imagining the hydrogen ion making transitions from its position of equilibrium in the neighborhood of a water molecule in the solution to a position of equilibrium on the surface of the glass; this latter position of equilibrium being at a level of equal or lower potential energy than the level in the solution. While some hydrogen ions are depositing on the glass, i.e., making d-transitions, other hydrogen ions on the surface of the glass having high enough energies will be dissolving, i.e., making s-transitions. At equilibrium the number of s-transitions must equal the number of d-transitions, and to obtain an equation for the interfacial potential it is only necessary to write down the number of s- and d-transitions and equate the two quantities. Let $U_H{}^{og}$ be the energy of the lowest quantum level of the hydrogen ion on the glass surface, $U_H{}^{os}$ the energy of the lowest quantum level of the hydrogen ion in the aqueous solution, $U_{Na}{}^{og}$ and $U_{Na}{}^{os}$ similar quantities for the sodium ion. We shall now suppose that owing to the interaction of neighboring molecules all energies above the ground level are possible vibration levels, in other words, all values of U between U^o and infinity are possible. We shall also assume that the distribution of the surface ions in their vibration levels is given by the Boltzmann law.

We shall first calculate the number of s-transitions, or rather the number of s-situations which is the number of situations or configurations that gives rise to an s-transition. Of the total number of surface ions per unit area of the glass, a fraction

$$(1/kT)\exp\{(U_H{}^{og}-U)/kT\}dU \qquad (2)$$

will have energies between U and $U+dU$ providing no interfacial potential exists. If an interfacial potential V does exist, the energy levels of the ions on the glass surface will be shifted relatively to those of the solution by the amount ϵV where ϵ is the unit positive charge. Taking the potential of the electrolyte as the zero of potential, expression (2) becomes

$$(1/kT)\exp\{(U_H{}^{og}+\epsilon V-U)/kT\}dU. \qquad (3)$$

The number of s-situations will also be proportional to N_w, the number of water molecules in contact with unit area of surface,

$$(N_w/kT)\exp\{(U_H{}^{og}+\epsilon V-U)/kT\}dU. \qquad (4)$$

However, part of the surface may be covered by sodium ions; this has the effect of diminishing the number of s-situations for the hydrogen ion. If we let γ represent the fraction of unit surface covered by hydrogen ions the number of s-situations now is

$$\gamma(N_w/kT)\exp\{(U_H{}^{og}+\epsilon V-U)/kT\}dU. \qquad (5a)$$

Similarly, the number of s-situations for the sodium ions is

$$(1-\gamma)(N_w/kT)\exp\{(U_{Na}{}^{og}+\epsilon V-U)/kT\}dU. \qquad (5b)$$

Up to this point we have assumed that the sodium and hydrogen ions can occupy the same number of lattice points on the surface of the glass; that is, we have assumed that a sodium ion can occupy any point occupied by a hydrogen ion and *vice versa*. But it is unnecessary to make this assumption. Let a equal the number of lattice points per unit surface which the hydrogen ion can occupy, then $a\gamma$ is the fraction of total possible lattice points occupied by hydrogen ions. The number of lattice points not occupied by hydrogen ions is equal to $a-\gamma a$ and of these we shall suppose that the sodium ions can occupy a fraction δ; $(a-\gamma a)\delta$ being the actual number of lattice points per unit surface occupied by the sodium ion. The quantity δ is independent of the concentration of the solution, but γ varies with the concentration. Eqs. (5a) and (5b) now become

$$a\gamma(N_w/kT)\exp\{(U_H{}^{og}+\epsilon V-U)/kT\}dU, \qquad (6a)$$

and

$$(a-\gamma a)\delta(N_w/kT)\exp\{(U_{Na}{}^{og}+\epsilon V-U)/kT\}dU. \qquad (6b)$$

The number of d-situations depends upon the number of ions in the solution N_H or N_{Na}, upon the energy of the ions and upon the number of lattice points on the glass surface that the ions can occupy; thus for the hydrogen and sodium ions we have

$$a(N_H/kT)\exp\{(U_H^{os}-U)/kT\}dU \quad (7a)$$

and $$a\delta(N_{Na}/kT)\exp\{(U_{Na}^{os}-U)/kT\}dU. \quad (7b)$$

It will be noticed that this treatment assumes that an ion can deposit on any of the possible lattice points whether or not the lattice point is already occupied. At equilibrium the number of s-situations multiplied by the probability of an s-transition must be equal to the number of d-situations multiplied by the probability of a d-transition. If the ratio of the latter probability to that of the former be β, then

$$a\gamma(N_w/kT)\exp\{(U_H^{od}+\epsilon V-U)/kT\}dU = \beta_H a(N_H/kT)\exp\{(U_H^{os}-U)/kT\}dU, \quad (8a)$$

$$(a-\gamma a)\delta(N_w/kT)\exp\{(U_{Na}^{od}+\epsilon V-U)/kT\}dU = \beta_{Na}a\delta(N_{Na}/kT)\exp\{(U_{Na}^{os}-U)/kT\}dU. \quad (8b)$$

Letting Q_H equal $(U_H^{os}-U_H^{od})$ and Q_{Na} equal $(U_{Na}^{os}-U_{Na}^{od})$ and setting N_H/N_w and N_{Na}/N_w equal to c_H and c_{Na}, respectively, Eqs. (8a) and (8b) become

$$\gamma = c_H\beta_H\exp(Q_H-\epsilon V)/kT, \quad (9a)$$

$$1-\gamma = c_{Na}\beta_{Na}\exp(Q_{Na}-\epsilon V)/kT. \quad (9b)$$

The quantity γ is easily eliminated from Eqs. (9a) and (b) by addition; we obtain

$$c_H\beta_H\exp(Q_H-\epsilon V)/kT+c_{Na}\beta_{Na}\exp(Q_{Na}-\epsilon V)/kT=1. \quad (10)$$

If there were no sodium ions present in the solution, the potential would depend solely on the concentration of hydrogen ions; from Eq. (10) we have, on setting c_{Na} equal to zero

$$V_0 = Q_H/\epsilon+(kT/\epsilon)\ln c_H\beta_H. \quad (11)$$

Eq. (11) is the usual hydrogen electrode potential equation since β_H is a factor of the order of magnitude of unity. The author originally defined the error of the glass electrode as being equal to $V-V_0$. This quantity may be obtained by dividing Eq. (10) (first putting it in its exponential form) by Eq. (11) and rearranging, the result being

$$V-V_0=(kT/\epsilon)\ln[(\beta_{Na}/\beta_H)c_{Na}\exp\{(Q_{Na}-Q_H)/kT\}+c_H]/c_H. \quad (12)$$

It is interesting to compare Eq. (12) with the previously derived Eq. (1). They are identical except that the constant factor multiplying the sodium ion concentration term has a different meaning in the two cases.

Resolution of the Glass Electrode Problems

This statistical treatment of the glass electrode immediately obviates the necessity of making any assumptions concerning the mobility of the hydrogen and sodium ions. Gurney's theory also provides us with a plausible explanation of the negligible effect of negative ions upon the glass electrode potentials. According to Zachariasen,[4] glass consists of a network of oxygen tetrahedra which surrounds the silicon atoms. The holes which necessarily exist in this framework are bounded by oxygen atoms or perhaps we should say by negative oxygen ions and offer excellent positions for positive ions. However, it is obvious that large repulsive forces would come into play if the attempt is made to introduce negative ions into these holes. Negative ions are also generally larger than positive ions which is another reason why it would be difficult to deposit negative ions on the glass surface. If we plot the potential energy of a negative ion as a function of distance along a line perpendicular to the glass surface, a figure similar to Fig. 1 would probably be obtained. By an inspection of Fig. 1 it is readily seen that negative ions in solution cannot make transitions to the glass surface because they do not have sufficiently high energies. Thus negative ions have no effect upon the glass electrode potentials, not because they have zero mobility, but because the energy relationships are not favorable.

From the experimental data it is possible to calculate that the order of magnitude of the constant which multiplies the concentration of the sodium ion in Eq. (1) is 10^{-11}, a figure which is not easily explained by the liquid junction theory.[5] This difficulty is fortunately considerably minimized if not entirely overcome by the statistical mechanical theory. Referring to Eq.

[4] W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

[5] Particularly since it is probably the hydrated proton and not the proton which moves across the glass-aqueous solution boundary.

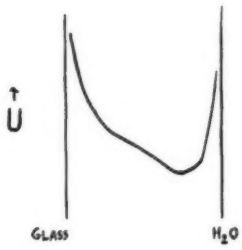


FIG. 1.

(12) it can be readily seen that the magnitude of the constant depends upon the magnitude of the term

$$\exp (Q_{Na}-Q_H)/kT, \qquad (13)$$

since β_{Na}/β_H is of the order of magnitude of unity. Calculation shows that expression (13) has the order of magnitude 10^{-11} when Q_H is greater than Q_{Na} by 15,000 calories per mole, an entirely plausible result. If experimental values of Q_H and Q_{Na} were known, it would be possible to test Eq. (12) quantitatively.

The final difficulty which is a stumbling block in the former liquid junction theory is due to the observation that the constant of Eq. (1) varies with the pH of the solution. It is hard to see why the mobility across the boundary should vary with the concentration of the aqueous solution. But let us examine the corresponding quantity in Eq. (12). Instead of the ratio of the mobilities we have the expression (13) whose magnitude is quite sensitive to the exponent $(Q_{Na}-Q_H)/kT$. If the glass were a metal, all ions of one kind on the metal surface would have the same value of U^o, but we would not expect this to be true for glass. Glasses in contrast to metals do not melt sharply but gradually soften over a range of temperature which indicates that ions in the glass do not have identical energies. To quote Zachariasen, "Since all atoms in glass are structurally unequivalent, the energy required to detach an atom from the net-work will be different for each individual atom." In acid solution the glass surface will be covered with hydrogen ions to the exclusion of sodium ions, but as the alkalinity of the solution increases some of the hydrogen ions will leave the glass surface; their places being taken by sodium ions. In all probability the remaining hydrogen ions will not have the same value of $U_H{}^{o_g}$. A small change in $U_H{}^{o_g}$ or in $U_{Na}{}^{o_g}$ would be sufficient to produce an appreciable change in the constant term of Eq. (12).

It should be emphasized, however, that until values of $U_H{}^{o_g}$ and $U_{Na}{}^{o_g}$ can be estimated this theory cannot be tested quantitatively.[6] Yet this new explanation seems to be much better than the former liquid junction theory.

CRITIQUE OF GROSS AND HALPERN'S THEORY

Gross and Halpern have recently interpreted the author's experimental data by assuming that glass may be treated as a difficultly soluble salt which forms with water a saturated solution and that the water dissolves in the glass until the glass becomes saturated with the water. They also assume that the mass action law holds for such strong electrolytes as sodium hydroxide and sodium acetate both in the water and glass phases, that water, glass, acids, bases, etc., distribute themselves between the glass and aqueous phases in accordance with the well-known distribution law and that the activity coefficients of all ions are the same. For alkaline solutions their equation reduces to

$$\Delta E=(RT/2F)\ln (1+c_{Na}{}^g/c_H{}^g), \qquad (14)$$

where c^g represents the ionic concentration *in the glass*. By assuming the validity of the distribution laws mentioned above it is possible to rearrange Eq. (14) into the form of Eq. (1) except that the factor RT/F of Eq. (1) is replaced by the factor $RT/2F$. For acid solutions Gross and Halpern succeed in deriving an equation identical with the acid solution equation previously derived by the author[7] with the exception that once again their equation contains the factor $RT/2F$ instead of the author's factor RT/F. Gross and Halpern claim that their equations agree with the author's data better than do the author's equations. Let us consider the acid solution data first. Gross and Halpern tested their Eq. (12) solely with the errors of the glass

[6] Eq. (12) may be tested quantitatively by measuring the temperature coefficient of $V-V_o$. Since the temperature appears in the exponential term multiplying the constant, the value of the glass electrode error should vary definitely with variation of temperature, the magnitude of the variation being quantitatively predicted by Eq. (12). Measurements of the temperature coefficient of the glass electrode are now in progress.

[7] M. Dole, J. Am. Chem. Soc. **54**, 3095 (1932).

electrode obtained in the ethanol solutions up to 66 percent ethanol and found slightly better agreement with their equation than with the author's. As a matter of fact, the alcohol experiments were not as accurate as the experiments, for example, measuring the error of the glass electrode in 4.4*N* lithium chloride. Over twenty measurements of the error of the glass electrode in 4.4*N* lithium chloride were obtained; one experiment yielded the following values of ΔE over the pH range 4.600 to 0.308, 5.1, 5.1, 7.4, 6.5, 9.3, 8.7, 7.6, 7.4, 7.2, 6.9, 7.2, 7.5 mv. From these and other data the best value of the error in 4.4*N* lithium chloride was taken as 6.7 mv. The error theoretically calculated by the author's equation is 7.0 mv. while Gross and Halpern's equation gives 3.5 mv. Gross and Halpern limited the test of their Eq. (12) to solutions having a water activity of 0.79 or greater. The activity of the water in 4.4*N* lithium chloride is 0.77. The experimental data for solutions in which the activity of the water is less than 0.77 also agree better with the author's equation than with the equation of Gross and Halpern.

Gross and Halpern's equation for the high pH range does not agree with the data as well as the author's unless the slope of the function is fixed at unity. This fact is made clear by reference to Fig. 2 where Gross and Halpern's function $\log [(\exp 2F\Delta E/RT)-1]$ and the author's function $\log [(\exp F\Delta E/RT)-1]$ are plotted against the pH. If one draws a straight line through the lowest three points in each case, the values of the functions at the higher pH values deviate farther from the straight line in the case of Gross and Halpern's function than in the case of the author's. However, if comparison is made with a line drawn with unit slope as demanded by former theory, dotted line of Fig. 2, it is evident that Gross and Halpern's function is superior, yet far from perfect. Fortunately the statistical

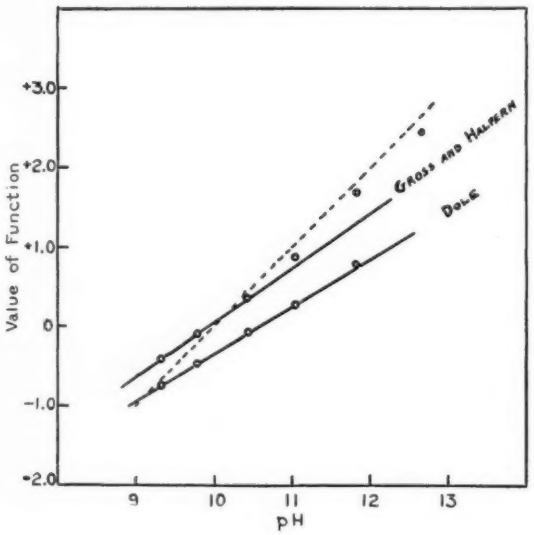


FIG. 2.

mechanical theory of the glass electrode does not demand a unit slope of the curves of Fig. 2.

Gross and Halpern's theory fails to give any explanation of the inability of negative ions to affect the glass electrode. Our new theory is decidedly superior in this respect.[8]

In conclusion the author wishes to acknowledge the kindness of Dr. R. W. Gurney in making available his unpublished treatment of the plating out of alloys and in discussing with the author the problems of the glass electrode.

[8] An interesting paper by Lengyel and Blum has recently appeared (Trans. Faraday Soc. **30**, 461 (1934)). They point out the significant relation between glass electrode behavior and composition of the glass. The ability of the glass electrode to act as a sodium electrode for certain types of glasses may be explained on the basis of our statistical theory by assuming that $Q_H - Q_{Na}$ has a negative or very small positive value. The Q values of this paper are not, however, the same as the Q values calculated by Lengyel and Blum. The latter represent the "heat of liberation" of the sodium ion in the glass whereas the author's Q values may be considered as being the difference between "the heat of liberation" in the aqueous solution and on the glass surface.

A Study of the Methods of Interpretation of Electron-Diffraction Photographs of Gas Molecules, with Results for Benzene and Carbon Tetrachloride

LINUS PAULING AND L. O. BROCKWAY, *Gates Chemical Laboratory, California Institute of Technology*

(Received September 17, 1934)

The reliability and accuracy of the visual method of interpreting electron-diffraction photographs, consisting in the correlation of values of $(4\pi \sin \vartheta/2)/\lambda$ obtained by visual measurement of rings of apparent maximum and minimum intensity with x values from a simplified theoretical curve (Eq. (7) or (8)), have been tested in the following ways: (a) The measurement and interpretation of "artificial electron-diffraction photographs" of bromine; (b) the comparison of electron-diffraction and band-spectral values of interatomic distances for bromine, chlorine and iodine chloride; (c) the study of microphotometer records for benzene, and comparison of results with those of the visual method; (d) the study of microphotometer records for carbon tetrachloride, and comparison with the visual method. It is concluded that the visual method when carefully applied leads to values of interatomic distances accurate to about 1 percent (probable error), or to ½ percent in favorable cases. The regular plane hexagon model of the benzene molecule is verified, the carbon-carbon distance in the ring being determined as 1.390±0.005A. The carbon-chlorine distance in the carbon tetrachloride molecule is determined as 1.760±0.005A. A brief discussion of the methods and results of other investigators is given.

THE investigation of the structure of gas molecules by the diffraction of electron waves was begun by Mark and Wierl[1] soon after the pioneer work of Debye[2] and co-workers on the diffraction of x-rays by gas molecules. The method has shown itself to be very useful, especially because the large scattering powers of atoms for electrons permit the use of very small exposure times (of a fraction of a second), and several groups of investigators (in the main with chemical interests) have entered the field. The recently discovered correlations of interatomic distances with electronic structure[3] and with force constants of bonds[4] have increased the interest in interatomic-distance measurements, and various other considerations, such as those regarding the angles between bonds, have emphasized the importance of determining accurately the configurations of many molecules. It is consequently desirable that the assumptions involved in the usual methods of interpretation of electron-diffraction photographs of gas molecules be critically examined, especially since these methods have received much unfavorable comment. We have carried out such an examination, using several independent and (we believe) objective checks on the usual method. Our results, described in this paper, show that a simple method of interpretation (involving the visual measurement of diameters of rings of apparent maximum and minimum intensity and the comparison with simplified theoretical curves) leads, when carefully carried out, to the determination of molecular configurations with a probable error of about ½ or 1 percent in the interatomic distances.

The general character of the following discussion of the theory and the correlated method of interpreting electron-diffraction photographs is determined by the nature of our interests. We are primarily concerned with developing a reliable method of determining interatomic distances which is simple enough to make practicable its application to a large number of compounds. The discussion of the theory in the next section indicates in part the arguments used by us in fixing on a particular procedure; it is not intended to be complete or rigorous. An attempt to establish the complete validity of the theoretical formulas for electron scattering would necessarily include the treatment of the incoherent scattering of electrons as well as the standardization of the photographic emulsions for electrons over a wide range of intensities, and the quantitative estimate of that part of the background intensity which is due to multiple scattering, to x-rays, and especially

[1] (a) H. Mark and R. Wierl, Naturwiss. **18**, 205, 778 (1930); (b) R. Wierl, Ann. d. Physik **8**, 521 (1931); (c) **13**, 453 (1932).
[2] P. Debye, Phys. Zeits. **30**, 524 (1929); **31**, 142, 348, 419 (1930); etc.
[3] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).
[4] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

to electrons scattered by gas in the diffraction chamber at points other than the intersection of the electron and gas beams. With this treatment quantitative agreement between calculated and observed intensities might be obtained. It would still be necessary, however, to resort to empirical tests in order to determine the sensitivity of the procedure as a method of finding interatomic distances.

We have chosen the visual treatment (for reasons given in the latter part of this paper) from among the various simplified procedures which are available. In view of the results reported below we believe that simplicity can be combined with accuracy in the use of electron diffraction as a method of determining interatomic distances.

A. Discussion of the Visual Method of Interpretation

Electron-diffraction photographs of gas molecules, obtained by the usual experimental methods,[5] show well-defined rings, making it appear that as the scattering angle increases the intensity of the scattered beam of electrons and the blackening of the photographic film pass through successive maximum and minimum values. This can be seen from the reproductions of Fig. 1, and much more clearly still on the original negatives, which may show as many as ten well-defined and measurable apparent maxima. The maxima and minima are not real, however, as was first pointed out by Wierl. Microphotometer records of three photographs are shown in Figs. 2 and 3. It is seen that the blackening of the film falls off monotonically from the center, the apparent maxima and minima on the photographs corresponding to fluctuations in the density about a rapidly falling background. It is a psychological or physiological phenomenon which causes the photographs to appear to show maxima and minima.

The character of the diffraction pattern as shown by the microphotometer records is in agreement with theoretical considerations. Debye[6] and Wierl[1] have shown that the intensity

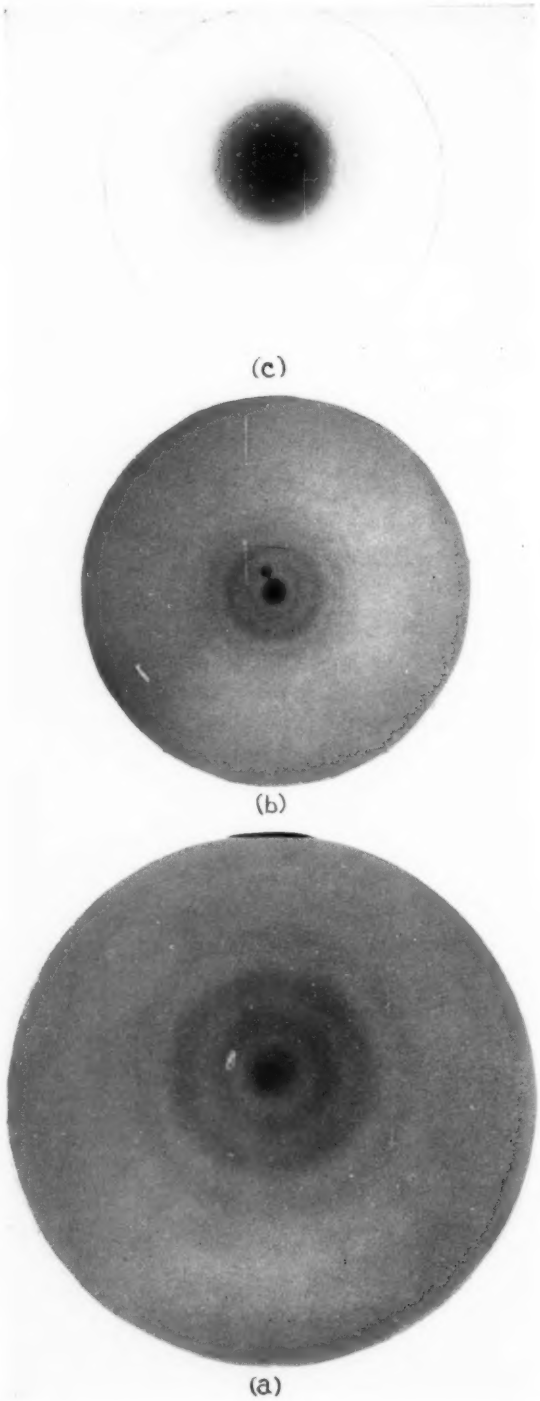


Fig. 1. Contact prints of electron-diffraction photographs. (a) Carbon tetrachloride at 28.7 cm. (b) Carbon tetrachloride at 12.19 cm. (The small spot to one side of the central image is due to visible light from the filament.) (c) Benzene at 12.19 cm.

[5] Such as described by Wierl.
[6] P. Debye, Ann. d. Physik **46**, 809 (1915).

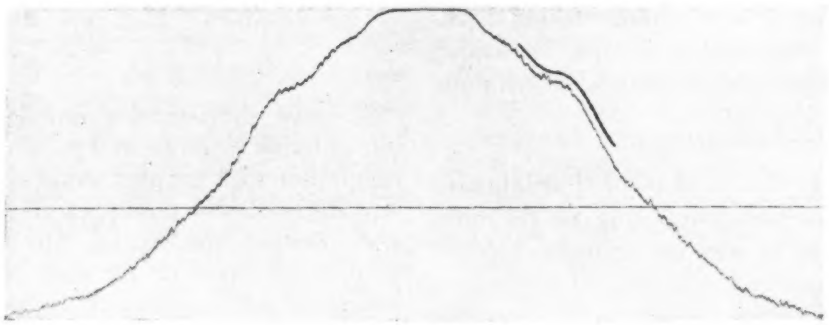
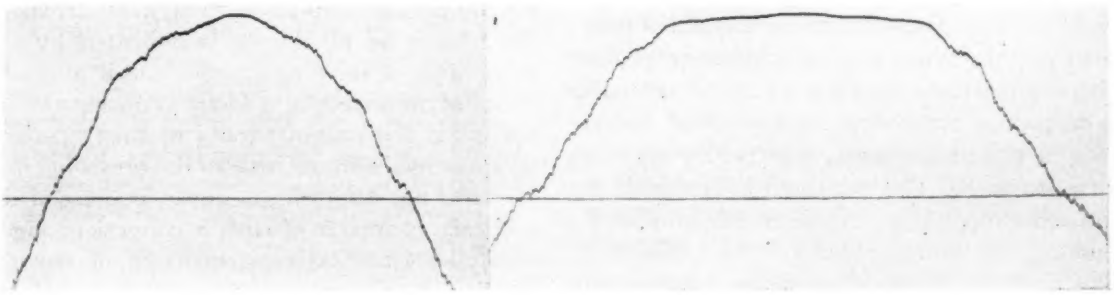


FIG. 2. Microphotometer record of a benzene photograph.



A B

FIG. 3. Microphotometer records of carbon tetrachloride photographs, (A) showing the first, second, and third apparent maxima, (B) showing the first five apparent maxima.

of the coherent electron scattering at the angle ϑ is given by the expression

$$I = k \cdot \sum_i \sum_j \psi_i \psi_j (\sin x_{ij})/x_{ij}, \tag{1}$$

in which k is a constant, and

$$x_{ij} = 4\pi l_{ij}((\sin \vartheta/2)/\lambda), \tag{2}$$

with l_{ij} the distance between atoms i and j in the molecule and λ the wave-length of the electrons. The quantity ψ_i is the scattering function of the i'th atom for electrons. It is approximated closely by the expression[7]

$$\psi_i = \frac{Z_i - f_i}{((\sin \vartheta/2)/\lambda)^2}, \tag{3}$$

in which Z_i represents the atomic number of the i'th atom and f_i its scattering factor for x-rays, which is essentially a function of $(\sin \vartheta/2)/\lambda$. Reasonably accurate values of f_i are known for all atoms; in our discussion we have used Pauling-Sherman f-values.[8] Now for convenience let us rewrite Eq. (1) as

$$I = I_{\text{atomic}} + I_{\text{molecular}}, \tag{4}$$

with

$$I_{\text{atomic}} = k \sum_i \psi_i^2 \tag{5}$$

and

$$I_{\text{molecular}} = k \sum_i \sum_j{}' \psi_i \psi_j (\sin x_{ij})/x_{ij}. \tag{6}$$

The summations in Eqs. (5) and (6) include all the atoms in a molecule, except that in 6 the terms $i=j$ are omitted, as indicated by the prime.

The nature of the scattering functions ψ_i is such that I_{atomic} decreases very rapidly with increase in scattering angle ϑ, the increase in $Z-f$ not being sufficient to overbalance that in $\sin^2 \vartheta/2$. Consequently the photographs are ex-

[7] H. Bethe, Ann. d. Physik **87**, 55 (1928); **5**, 325 (1930); N. F. Mott, Proc. Cambridge Phil. Soc. **25**, 304 (1929).

[8] L. Pauling and J. Sherman, Z. Krist. **81**, 1 (1932).

pected to show a very rapidly falling background, with fluctuations in the blackening about this background in accordance with the $\frac{\sin x}{x}$ functions of $I_{\text{molecular}}$.

Hence the correlation of theoretical intensity curves and observed blackening of the films cannot be made by any such simple objective method as comparing maxima and minima on the theoretical curves with those on the microphotometer records; to interpret the microphotometer records some more laborious procedure must be adopted, such as quantitative comparison over a wide angular range. In order to avoid any such time-consuming method of treatment as this, Wierl devised a simple expedient whereby the theoretical curves are so altered as to reproduce approximately the visual appearance of the photographs, with which they are then compared. This consisted in replacing the scattering function ψ_i by the atomic number Z_i, ignoring the term f_i and the factor $1/(\sin^2 \vartheta/2)$. The resultant curve then shows maxima and minima, which Wierl (and succeeding investigators) identified with the apparent maxima and minima in order to determine the structure of the molecule and to evaluate the interatomic distances.

This drastic simplification, which was given by Wierl without justification, other than the remark that the eye corrects for the effect of the factor $\csc^4 \vartheta/2$, can be made to appear reasonable by the following argument.

It is known that the sensitivity of the eye to change in stimulus is determined by the magnitude of the total stimulus, a change by a constant fraction of the total being detectable over a wide range of magnitudes of the total stimulus (Weber-Fechner law). It is accordingly not unreasonable for us to make the postulate that on the electron-diffraction photographs the eye detects fluctuations about a background to an extent determined by the ratio of the fluctuations to the background. Moreover, we assume for these considerations that the background is the function I_{atomic}, which falls off smoothly with increasing scattering angle. The apparent intensity of scattering we may then express as

$$I_{\text{apparent}} = \frac{I_{\text{molecular}}}{I_{\text{atomic}}} = \frac{\sum_i \sum_j{}' \psi_i \psi_j (\sin x_{ij})/x_{ij}}{\sum_i \psi_i^2}. \quad (7)$$

A curve showing this function for carbon tetrachloride is given in Fig. 4. It is seen on comparison with the photographs that this curve reproduces closely the appearance of the rings. For example, the second, fifth, seventh and tenth rings appear on the photographs to be as strong as the immediately preceding rings, or even somewhat stronger, in agreement with the calculated function (this phenomenon arising from the reinforcement of the carbon-chlorine and chlorine-chlorine terms). The function of Eq. (7) does not fall off in value with increasing angle quite as rapidly as is indicated by the appearance of the photographs, and it might be desirable to introduce a factor reducing the intensity at the rate of twenty or thirty percent for each maximum relative to the preceding one. We have not done this, however, because of the arbitrary character of such a correction; moreover, the quantitative comparison of maxima and minima would not be changed appreciably by this procedure (within about one-tenth of one percent).

We may emphasize the fact that the postulate underlying Eq. (7) is more definite than is necessary for the visual interpretation of the photographs in a satisfactory manner. The simple assumption that the eye observes the fluctua-

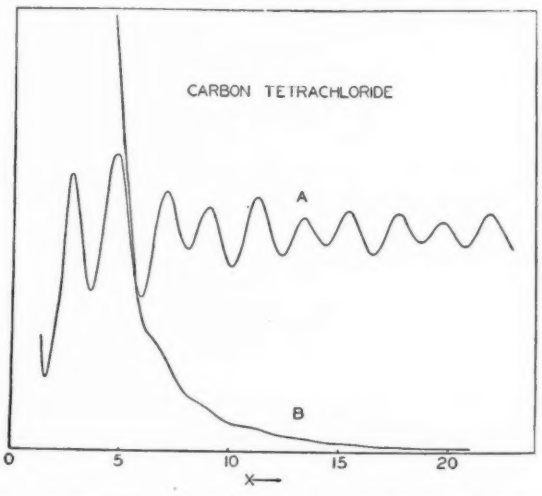


FIG. 4. The complete theoretical curve for carbon tetrachloride (B) and the simplified theoretical curve (A).

tions about the smooth background I_{atomic} with an apparent intensity lying somewhere between the actual intensity of the fluctuations (as given by Eq. (6) for $I_{\text{molecular}}$) and the intensity relative to the background (as in Eq. (7)) fixes the positions of the maxima and minima to within about 0.2 percent, after the first two maxima, for which the error is somewhat larger. This constancy in position of the maxima and minima, despite the fact that the magnitude of the fluctuations as given by Eq. (6) falls off from the first to the tenth maximum to one-thousandth of the value given by Eq. (7), results from the fixed position of the zeros of these two limiting curves and of all intermediate curves.

A further simplification in the calculation, leading to Wierl's treatment, can usually be made. If the molecule contains atoms of only one kind (Br_2, P_4, etc.) the terms Z_i-f_i in numerator and denominator of Eq. (7) cancel, so that the expression is exactly the same as Wierl's expression

$$I_{\text{apparent}}=\sum_i\sum_j Z_iZ_j(\sin x_{ij})/x_{ij}, \qquad (8)$$

except for a constant factor and an additive constant, both of which are unimportant in the simplified procedure. Moreover, Eq. (7) reduces to 8 whenever the ratios $(Z_i-f_i)/Z_i$ are constant for all atoms in the molecule. These ratios are found to be roughly constant for most atoms. For example, for $(\sin \vartheta/2)/\lambda=0.4$ the ratio has the values 0.87 for H, 0.61 to 0.69 for B to F, 0.46 to 0.51 for Al to Cl, and 0.39 to 0.42 for Ga to Br. Hence Eq. (8) can be safely used whenever the molecule contains only atoms from one row of the periodic table. Indeed, the error involved in even the most extreme cases is negligible in comparison with the limits of error inherent in the method at present, the positions of the maxima and minima never being shifted by more than a fraction of one percent, so that the simple expression (8) can almost always be used.

B. Tests of the Visual Method of Interpretation

In order to obtain information as to the accuracy and reliability of the visual method of interpretation of electron-diffraction photographs, involving the evaluation of interatomic distances through the quantitative identification of maxima and minima of the functions of Eq. (7) or (8) with the apparent maxima and minima on the photographs, we have carried out an extensive series of tests of various kinds. The nature of these and the results obtained are discussed in the following paragraphs.

A detailed description of our standard procedure is given in Section C.

I. The measurement of artificial photographs of Br_2

To test the fundamental postulate underlying the visual method of interpretation (Eq. (7)), we first prepared and measured "artificial electron-diffraction photographs." (This was done at the suggestion of Professor R. M. Badger, to whom we wish to express our thanks.) The complete intensity curve (neglecting incoherent scattering) was calculated for the bromine molecule, Br_2, with the Br-Br distance 2.280A, using Eqs. (1) and (3) and Pauling-Sherman f-values. The portion of this curve including the region from the first maximum to the fourth minimum of the $(\sin x)/x$ function was then plotted on a large scale in polar coordinates (25 cm radius) in such a way that the intensity was represented by the length of the arc at the radius determined by the value of $(\sin \vartheta/2)/\lambda$, this portion of the arc being blackened. This drawing was then photographed on a process plate, to produce a mask. By passing light through this mask onto a photographic film rotating about its center, the film was subjected to the action of light of integrated intensity (at different distances from the center) represented by the original theoretical intensity curve for the bromine molecule, and the blackening of the film would correspond to this function except for the correction due to the characteristics of the emulsion for visible light. The resultant artificial electron-diffraction photograph was about 6 cm in diameter, corresponding to a gas-stream-to-film distance of about 30 cm for electron wave-length 0.06A. The photograph showed two well-defined minima and two maxima (the second and third of each), and closely resembled real electron-diffraction photographs of bromine.

At the time these photographs were prepared we were interested in the possibility of the existence of apparent maxima and minima (on visual examination) on photographs in which the density falls off monotonically from the center. This decrease would remain monotonic for any monotonic relation between photographic density and intensity of incident light, and so it was not necessary for us to correct the mask for the characteristics of the emulsion. The density of the photographs consequently did not reproduce exactly the calculated intensity curve. It is of interest, however, that measurements of the diameters of these apparent maxima and minima (which were reproducible to within one percent) led on comparison with the simple $(\sin x)/x$ curve (of Eqs. (7) and (8)) to the value Br-Br = 2.30A. This value, which is one percent larger than the assumed value 2.28A, lends support to the method of interpretation.

II. The comparison of electron-diffraction and band-spectral determinations of interatomic distances

A straightforward test of the accuracy of the electron-diffraction method can be made by comparing interatomic distances determined in this way with the values found from the rotational fine structure of band spectra. We have carried out this comparison for bromine in detail, and have made a similar but less thorough study of chlorine and iodine chloride.

The Br–Br internuclear separation in Br_2 is known[9] to have the value 2.281A (the average for the zeroth vibrational state). We found bromine vapor to produce satisfactory electron-diffraction photographs, on which (as a rule) five well-defined rings appeared. The calibration of the apparatus was carried out with gold foil, for which the value $a_0 = 4.070$A for the edge of the unit of structure was adopted. Measured values of $(4\pi \sin \vartheta/2)/\lambda$ for four apparent minima and five apparent maxima on one such bromine photograph are given in Table I. Each value is the average of three measurements, which with few exceptions lay within one-half percent of their mean. The first minimum could not be measured with any accuracy. By comparing these with the values of x for which the function $(\sin x)/x$ shows its maxima and minima, the values given for the Br–Br distance were calculated. It is seen that except for the first one these values do not differ individually from their average by more than 0.02A or one percent. We have found through experience that the measurements of the innermost rings are not very reproducible and are unreliable, the interatomic distances calculated for them from measurements made under standard conditions adopted by us showing deviations of several percent from the values given by the outer rings. For this reason we ordinarily discard measurements of the first maximum and second minimum. This has been done in taking the average in Table I.

TABLE I. *Measurement of photograph 375 of Br_2.*

Maximum	Minimum	x	$\frac{4\pi \sin \vartheta/2}{\lambda}$ observed	Br–Br
1		7.725	3.48	(2.22A)
	2	10.904	4.82	(2.264)
2		14.066	6.18	2.279
	3	17.221	7.56	2.278
3		20.371	8.89	2.292
	4	23.520	10.32	2.279
4		26.666	11.67	2.287
	5	29.81	12.96	2.302
5		32.96	14.48	2.278
			Average of seven	**2.285A**

In Table II there are given the averaged results for seven photographs, the last three of which were somewhat less distinct than the others, permitting a smaller number of measurements. It is seen that the seven average values lie within a total range of 0.7 percent. The average of all the values is 2.289A, the least-squares probable error being 0.0015A. The actual

TABLE II. *Results of seven Br_2 photographs.*

Photograph No.	Number of rings measured	Average Br–Br	Photograph No.	Number of rings measured	Average Br–Br
375	7	2.285A	394	6	2.285A
376	7	2.284	393	5	2.299
377	7	2.293	378	5	2.295
392	7	2.290	Average of measurements		**2.289A**

[9] W. G. Brown, Phys. Rev. **29**, 777 (1932). Brown reported r_0 as 2.28A; the value 2.281A is calculated from his more accurately reported moments of inertia.

error, accepting the band-spectral value 2.281A as correct, is 0.008A.

Somewhat less satisfactory photographs have been obtained for chlorine and for iodine chloride. For chlorine four photographs, each showing four apparent maxima, were measured, the average value of the Cl–Cl distance provided by them being 2.009A, with an average deviation of 0.015A. This value is one percent larger than the band-spectral value[10] 1.988A. Three rather poor photographs of iodine chloride gave for the I–Cl distance the average value 2.301A, with an average deviation of 0.010A. This is slightly smaller than the band-spectral value[11] 2.315A. We intend to continue the study of these compounds.

The electron-diffraction photographs used in this treatment of the three substances are of about average quality. The actual errors in the interatomic distances found from them (accepting the band-spectral values as accurate) are +0.4, +1.1 and −0.6 percent. From these results we draw the conclusion that the probable error of interatomic distances determined in this way from electron-diffraction photographs is of the order of magnitude of one percent.

III. The study of microphotometer records for benzene

The electron-diffraction photographs of benzene show several apparent maxima and minima, of which one (the second maximum) is very prominent. It appears on the microphotometer records (Fig. 2) as a well-defined shoulder, the slope nearly reaching zero. The microphotometer record shows, however, no single feature which can be quantitatively identified with confidence with a corresponding feature on the theoretical intensity curve. In order to obtain a value for the size of the molecule from the microphotometer records we have adopted the following procedure. The microphotometer was first calibrated for x-radiation, using time of exposure as a measure of integrated incident intensity. We have assumed that the behavior of the film towards fast electrons is sufficiently closely similar to that towards x-rays to permit this calibration to be used for electron-diffraction photographs also. On comparison of the benzene photographs with the theoretical intensity expression, it was found that the photographs showed additional blackening; that is, there is present, aside from the diffraction pattern, a background, which probably is due to incoherently-scattered electrons, to electrons scattered by gas molecules in the body of the apparatus, to multiple scattering, and to other causes. Inside of the shoulder the background is unimportant (amounting to less than half the total intensity at the left end of the segment of curve drawn in Fig. 2), whereas outside of the shoulder the background is stronger than the diffraction pattern (amounting to three-quarters of the total intensity at the right end of the segment).

It was found that by adding a constant background intensity of suitable magnitude to the intensity expression of Eqs. (1) and (3) and by making use of the calibration of the microphotometer, a theoretical microphotometer curve for benzene could be calculated which could be closely fitted to the observed curves over a considerable region including the pronounced shoulder. One such curve is shown in Fig. 2. In calculating these curves the intensity expression including the atomic scattering factors ψ_i was used, with Pauling-Sherman f-values. The regular plane hexagonal model of benzene was assumed, the ratio of the C–H to C–C distances being taken as 1.06 to 1.38 (a small change in this ratio would not change the curves appreciably). The curves were plotted on a scale corresponding to a C–C distance of about 1.38–1.40A. On superimposing such a curve on a microphotometer record, it was found in general that a satisfactory fit was obtained only by moving the curve towards or away from the center. The amount of this translation (for both branches of the curve) was measured, and from it there was calculated a new value for the carbon-carbon distance, the proper corrections being applied (for shrinkage of the print of the microphotometer record, etc.).

[10] Recalculated by Professor R. M. Badger from the data of A. Elliott, Proc. Roy. Soc. **A123**, 629 (1929); **A127**, 638 (1930).

[11] W. E. Curtis and J. Patkowski, Phil. Trans. Roy. Soc. **A232**, 395 (1933). The smaller value 2.306A was given by these authors in an earlier note (Nature **127**, 707 (1931)) which is not mentioned by them in their later paper.

In order to study the reliability of this procedure, various assumptions regarding the nature of the background were tried out. It was found that the background could be assumed to be constant, or to fall off linearly from the center, or to change in accordance with some other simple relation not deviating greatly from a constant value. When the theoretical curve for incoherent scattering was tried as the background no satisfactory fit of the theoretical microphotometer curve and the observed records could be obtained, the incoherent scattering falling off too rapidly from the center. This shows that the other background effects mentioned above are too important to be neglected in a quantitative comparison of theoretical and observed intensities. Whenever a satisfactory fit of the theoretical curve with the observed records could be obtained, the same size (to within about $\frac{1}{2}$ percent) was calculated for the molecule.

The results of the application of this procedure are given in Table III. It is seen that from the

TABLE III. *Results of study of microphotometer records for benzene.*

Film and plate	Number of curves used	Number of measurements	Average C–C distance	Average deviation
263 P17	5	14	1.395A	0.005A
264 P 6	6	10	1.388	.003
264 P20	5	17	1.386	.005
269 P 8	5	10	1.391	.002
269 P21	4	14	1.385	.005
Average of 65 measurements			**1.389A**	

consistency of measurements made with different background expressions, different films, and different microphotometer records the average value 1.389A for the carbon-carbon distance should be considered as very accurate, the least-squares probable error being only about ±0.001A for each film and plate and also for the average of the five entries in the table.

IV. The visual interpretation of benzene photographs

The visual treatment of the photographs was made in the usual way. The theoretical curve for apparent intensity as given by Eq. (7) is shown in Fig. 5, calculated for the distances C–H=1.06A and C–C=1.380A. (The simple

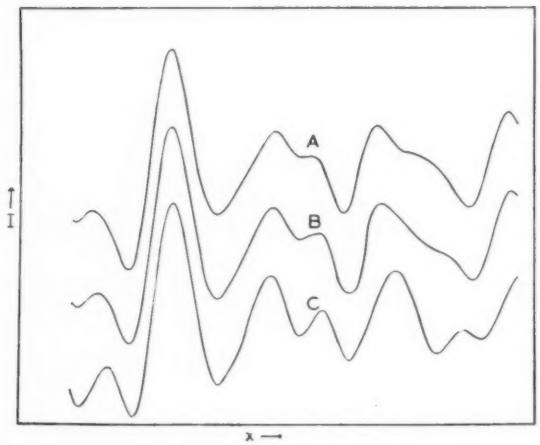


FIG. 5. The simplified theoretical curves for benzene. *A*, Plane hexagon model. *B*, Carbon atoms staggered to 0.1A above and below the original plane. *C*, Carbon atoms staggered to 0.2A.

curve of Eq. (8) is almost indistinguishable from this.) The qualitative agreement of the photographs and the curve is good. The films show a weak first maximum and a strong second maximum. These are followed by a poorly-defined third minimum and a broad third maximum showing a shelf on its outer edge. Then come a very narrow and distinct fourth minimum and a sharp fourth maximum. On some films a fifth minimum and maximum can also be seen.

Results of the measurement of one photograph are given in Table IV. Each observed value of

TABLE IV. *Visual measurements of photograph 264 for benzene.* $\lambda=0.0599$A.

Maximum	Minimum	$\frac{4\pi \sin \vartheta/2}{\lambda}$ observed	x for 1.380A	C–C
1		3.35	2.84	1.17A
	2	4.39	4.23	1.33
2		5.805	5.86	1.392
	3	7.56	7.66	1.398
3		9.55	9.96	1.439
	4	12.61	12.60	1.379
4		13.83	13.91	1.388

$(4\pi \sin \vartheta/2)/\lambda$ is the mean of from three to five measurements, which in most cases lie within a total range of one percent. The first maximum and second minimum, as usual, lead to low values for the size of the molecule. The third minimum and third maximum were

poorly defined, and we consider them unsuited for quantitative use. The fourth minimum and maximum were very easily and reproducibly measured. We consider that they and the second maximum should be used for the determination of the size of the molecule.

The results of measurements on ten photographs of benzene are given in Table V. It is

TABLE V. *Results of visual measurement of benzene photographs.*

Photograph	λ	Carbon-carbon distance from Second maximum	Fourth minimum	Fourth maximum
264	0.0599A	1.392A	1.379A	1.388A
269	.0602	1.391	1.372	1.380
263	.0599	1.387	1.387	1.402
265	.0632	1.403	1.375	1.406
268	.0602	1.400	1.389	1.383
315	.0614	1.388	1.368	1.395
316	.0614	1.403	1.389	1.400
317	.0614	1.403	1.387	1.399
318	.0614	1.392	1.369	1.395
319	.0614	1.408	1.390	1.406
Average		1.397A	1.381A	1.395A
Average of all values			**1.391A**	

seen that the results from the various photographs are concordant, the average deviation of the thirty values from the mean being 0.009A. There is evidently a constant error in opposite directions for the minimum and the two maxima (probably due to a small St. John effect), causing a difference of one percent in the averages calculated. If we accept the result of the microphotometer treatment, the error affects each to about one-half percent.

The average carbon-carbon distance given by the thirty measurements is 1.391A. This agrees excellently with the value 1.389A obtained from the much more objective discussion of the microphotometer records. We believe that the value 1.390A can be accepted for the carbon-carbon distance in the benzene molecule, with a probable error of about 0.005A.

V. The study of microphotometer records for carbon tetrachloride

When the attempt was made to treat the microphotometer records of carbon tetrachloride in the same way as those of benzene, it was found that the small amplitudes of the undulations prevented the procedure from being carried out with the desired accuracy of one or two percent. In consequence another treatment was used. This treatment, which depends for its success on the regularity of the undulations corresponding to the successive apparent maxima and minima, consists in drawing three smooth curves, two of which just touch the microphotometer curve at the extreme points of the undulations, the third being midway between them. It is then assumed that the middle curve represents the intensity aside from the $(\sin x)/x$ terms of Eq. (6), and that the points of intersection of this curve with the microphotometer curve are the points at which the function of Eq. (6) passes through the value zero. The results of this identification are given in Table VIA, each

TABLE VI. *Measurements of microphotometer record 281 P26 of carbon tetrachloride.*

A. Measurement of midpoints of undulations

Midpoint	$\frac{4\pi \sin \vartheta/2}{\lambda}$ measured	x for 1.80A	C–Cl distance
6	6.59	6.50	1.775A
7	7.68	7.66	1.795
8	8.71	8.49	1.755
9	9.78	9.45	1.740
10	10.87	10.65	1.765
11	12.14	11.85	1.757
12	13.40	13.00	1.747
		Average	**1.762A**

B. Measurement of extreme points of undulations

Maximum	Minimum	$\frac{4\pi \sin \vartheta/2}{\lambda}$ measured	x for 1.80A	C–Cl distance
3		7.21	7.00	1.747A
	3	8.27	7.97	1.735
4		9.37	9.00	1.731
	4	10.18	10.00	1.776
5		11.50	11.20	1.750
	5	12.66	12.36	1.757
6		13.66	13.32	1.754
			Average	**1.750A**

value reported for $(4\pi \sin \vartheta/2)/\lambda$ being the average from two independent constructions. It was also assumed that the points of contact of the other two curves and the microphotometer curve correspond to the maxima and minima of the function of Eq. (6). The results for these curves are given in Table VIB.

The values C–Cl = 1.762A and 1.750A from this treatment we estimate to be reliable to about ±0.02A, the average deviation from the mean in the two cases being 0.014A and 0.011A. The agreement with the visual treatment is

satisfactory, the visual measurements of this photograph (discussed in the next section) yielding the value C–Cl = 1.750A (average of ten maxima and minima with an average deviation of 0.009A), and the average for all photographs being 1.760A.

VI. The visual interpretation of carbon tetrachloride photographs

We have obtained very good electron-diffraction photographs of carbon tetrachloride, on some of which twenty apparent minima and maxima could be seen and measured. As mentioned before, the qualitative appearance of these photographs is in excellent concordance with the curve of Fig. 4 calculated from Eq. (7). The diameters of the rings of apparent maximum and minimum intensity were measured on nineteen photographs taken at the film distance 12.19 cm and with various electron wavelengths. In accordance with our standard practice, three series of measurements of ring diameters were made for each photograph, and the results averaged to give the observed value of $(4\pi \sin \vartheta/2)/\lambda$.

The results of this treatment for one photograph (No. 282) are given in Table VII. The individual ring-diameter measurements usually lay within one-half percent of their mean; for example, for this photograph the readings in centimeters for some rings are: fourth maximum, 2.187, 2.192, 2.177; fifth minimum, 2.437, 2.438, 2.438; fifth maximum, 2.694, 2.690, 2.690; sixth minimum, 2.969, 2.970, 2.983; etc. The values of x corresponding to the maxima and minima on the curve calculated for an assumed C–Cl distance of 1.800A are given in Table VII. From these and the observed $(4\pi \sin \vartheta/2)/\lambda$ values there are calculated the values of the C–Cl distance given in the last column.

TABLE VII. *Results of visual treatment of photograph 282 of carbon tetrachloride.* $\lambda = 0.0609$A.

Maximum	Minimum	$\frac{4\pi \sin \vartheta/2}{\lambda}$ observed	x for 1.800A	C–Cl distance
1		2.93	2.67	(1.64A)
	2	3.83	3.57	(1.68)
2		4.91	4.71	(1.728)
	3	6.00	5.90	1.770
3		7.13	7.00	1.767
	4	8.14	8.04	1.777
4		9.23	9.01	1.757
	5	10.28	10.05	1.761
5		11.34	11.22	1.780
	6	12.53	12.35	1.773
6		13.54	13.39	1.780
	7	14.61	14.39	1.771
7		15.79	15.42	1.759
	8	16.81	16.55	1.771
8		17.82	17.70	1.788
	9	18.90	18.77	1.787
9		19.98	19.73	1.777
	10	21.22	20.70	1.756
10		22.34	21.86	1.762
			Average	**1.771A**

We have found that on the 12.19 cm photographs the inner rings are not reliable, the interatomic distances calculated from them being usually too small. This is illustrated by the first three values of Table VII, which we discard. The following sixteen values are satisfactorily constant, showing a maximum deviation of only one percent from their mean. The average of the sixteen values is 1.771A, with an average deviation from this of 0.009A and a least-squares probable error of 0.0017A.

The results of a similar treatment of all nineteen photographs are contained in Table VIII. In each case the value given is the average for a series of rings (each measured in triplicate) beginning at about the third minimum and ending at the place where the photograph became indistinct. The values are reasonably consistent,

TABLE VIII. *Results of visual treatment of nineteen carbon tetrachloride photographs.*

Photograph number	λ	Number of rings	Average C–Cl distance
243	0.0609A	6	1.748A
244	.0609	9	1.754
245	.0609	6	1.747
271	.0611	10	1.768
274	.0611	6	1.728
279	.0609	11	1.770
280	.0609	15	1.756
281	.0609	10	1.750
282	.0609	16	1.771
347	.0619	12	1.737
348	.0619	11	1.731
356	.0619	14	1.781
357	.0619	8	1.769
P.1	.0609	8	1.800
365	.0604	8	1.759
366	.0604	8	1.753
367	.0604	10	1.757
368	.0604	8	1.769
369	.0617	8	1.777
		Weighted average*	**1.760A**

* Weighted with the numbers in the third column.

though not so consistent as those from the various rings of a single photograph. We think it probable that there is some error in the wavelength values resulting from uncertainty as to the accelerating potential at the instant of exposure.

The average for the 184 measured rings is 1.760A. The average for the nineteen photographs is 1.759A, with an average deviation of 0.014A and a least-squares probable error of 0.0026A. The average for the nine most distinct photographs, those with ten or more useful rings, is 1.758A, with an average deviation of 0.013A. In view of these results, and those of the previous section, we write for the carbon-chlorine distance C–Cl = 1.760A, with a probable error of about 0.005A.

C. Conclusions Regarding the Visual Method of Interpretation

From the results of the various tests described in the preceding sections we conclude that the visual method of interpretation of electron-diffraction photographs, when carefully carried out, can be relied on to lead to values of interatomic distances which in many cases are accurate to within about one-half percent as probable error.

In our standardized procedure the photographs are usually prepared with electron wavelength about 0.06A and the distance from gas stream to film equal to about 12 cm (or in some cases 20 cm or 30 cm). The diameters of rings of apparent maximum and minimum intensity are then measured on a specially designed comparator, consisting of an illuminated opal glass plate on which the negative is mounted and of two pointers which are moved independently by micrometer screws. The ring diameters are read directly on a vernier and scale mounted on the carriages which support the pointers. The average of several readings of each diameter is used for the calculation of the value of $(4\pi \sin \vartheta/2)/\lambda$. In the interpretation of the photographs our first step is to attempt to decide among various reasonable models by the qualitative comparison of the simplified theoretical curves calculated for them and the visual appearance of the photographs. This qualitative comparison is sometimes more effective in the selection of the correct model than the quantitative comparison. The interatomic distances for the selected model are then found by the comparison of the values of $(4\pi \sin \theta/2)/\lambda$ and of x, the choice among alternatives sometimes being made by the consideration of the mutual consistency of these values.

We have found that on short-distance photographs of some substances rings close to the central image (that is, about 1 cm in diameter) have apparent diameters corresponding to too small values of the interatomic distances. The effect is not observed, however, when the first ring lies farther out, as in the case of photographs of molecules of small dimensions (for example, carbon tetrafluoride, silicon tetrafluoride), and also in the case of photographs of most other substances taken at greater camera distances. This is probably a contrast effect of the dense central image on visual measurements made close to it.

In the application of the visual method consideration must also be given the fact that the measured diameters for unsymmetrical apparent maxima and minima do not correspond exactly to the maxima and minima of the simplified theoretical curve, as a result of the St. John effect. This effect causes the two components of a double maximum to be read with too large a separation. An apparent maximum with an outer shelf gives a small measured ring diameter, corresponding to too large an interatomic distance, and an apparent maximum with an inner shelf shows an error in the opposite direction. We propose to make a thorough study of this phenomenon, with the view of formulating a method of correction. At the present time the procedure which we recommend is to ignore interatomic-distance values given by very unsymmetric apparent maxima and minima in calculating the averaged interatomic distances for a molecule, and to include the values for the less unsymmetric ones, with the hope that the errors will to some extent cancel in the averaging.

The photographs of benzene show this phenomenon in a pronounced form. The broad third maximum shows an outer shelf, as a result of which the ring diameter as measured is

three or four percent too small. (In other cases this error may be as great as ten percent.) The fourth minimum and fourth maximum seem also to show a very small St. John effect, amounting to about one-half percent, as mentioned before.

It is our belief that the most reliable method of obtaining molecular sizes from electron-diffraction photographs at present is the objective method we have applied to benzene, consisting in matching over a considerable range a theoretical microphotometer curve and an actual microphotometer record. This method can be applied, however, only when the microphotometer record shows very pronounced reverse curves, as for benzene. We consider that whenever the photographs show several well-shaped apparent maxima and minima the visual method is reliable for the determination of interatomic distances, as mentioned above, and that, moreover, the qualitative and quantitative application of the visual method provides by far the most satisfactory basis of choice among several models for a molecule. An important advantage of the visual method is that it permits use to be made of a larger angular range of the diffraction pattern (for the qualitative comparison) and of a larger number of measured ring diameters (for the quantitative comparison) than the methods based on microphotometer records.

In our opinion the various hybrid methods of interpretation, such as, for example, the correlation of single points on a microphotometer record with points on a theoretical curve as applied by us to carbon tetrachloride in Section V, are less reliable than the visual method. Other examples of such methods are mentioned in the last section of this paper. Until these methods have been shown to lead to consistent and correct results, we feel that they are unreliable.

The Structure of the Benzene Molecule

In the foregoing discussion we have assumed, in view of various experimental and theoretical arguments, that the equilibrium positions of the six carbon atoms of the benzene molecule are at the corners of a regular plane hexagon. The qualitative agreement of the electron-diffraction photographs with the theoretical curve for this model (curve *A* of Fig. 5) supports this assumption. In order to find the extent of this support, we have calculated similar curves for a puckered hexagonal model; namely, curve *B* for a displacement of 0.1A above and below the original plane (corresponding to a bond angle of 118°), and curve *C* for a displacement of 0.2A (corresponding to a bond angle of 112°). Curve *C* is in definite disagreement with the appearance of the photographs, and curve *B* is somewhat less satisfactory than *A*. The principal feature of comparison is the third observed apparent maximum, which on the photographs shows an outer shelf, but does not appear as a double ring. Consequently we conclude that the electron-diffraction photographs require the benzene ring to show no puckering greater than corresponding to curve *B*.

Our value for the carbon-carbon distance, 1.390 ± 0.005A, agrees with the less accurate value of Wierl, given by him as 1.39 ± 0.03A[1b] or 1.40 ± 0.03A.[1c] So far as we know, no value from x-ray diffraction by gas molecules has been reported, though the investigation of benzene has been mentioned by workers in this field.[12]

It is probable that the carbon-carbon distance in the benzene ring retains the value 1.390A (to within about 0.01A) in benzene derivatives. It has been customary in recent years to quote the value 1.42A (as in graphite), on the basis of the x-ray investigation of crystals of hexamethylbenzene[13] and durene[14] (sym. tetramethylbenzene). The values found for these substances, 1.42 ± 0.03A and 1.41A, are probably in agreement with our lower value to within their experimental error. In aromatic molecules with condensed benzene rings we expect the carbon-carbon distance to lie between the benzene value and the graphite value, as is true of the values reported for naphthalene,[15a] anthracene,[15b] and chrysene,[16] which are 1.40–1.41A, 1.41A, and 1.41A, respectively.

[12] L. Bewilogua, Phys. Zeits. **32**, 114 (1931); **33**, 688 (1932).
[13] K. Lonsdale, Proc. Roy. Soc. **A123**, 494 (1929).
[14] J. M. Robertson, Proc. Roy. Soc. **A141**, 594 (1933); **A142**, 659 (1933).
[15a] J. M. Robertson, Proc. Roy. Soc. **A142**, 674 (1933); [b] **A140**, 79 (1933).
[16] J. Iball, Proc. Roy. Soc. **A146**, 140 (1934).

The Structure of Carbon Tetrachloride

Our photographs are in complete agreement with the regular tetrahedral model of the carbon tetrachloride molecule.

The chlorine-chlorine distance in carbon tetrachloride was reported by Debye and his collaborators to have the value 3.3A,[17] 3.1A,[18a] and finally 2.99±0.03A,[18b] the last of these corresponding to a carbon-chlorine distance of 1.83 ±0.02A. In regard to the 4 percent discrepancy between this value and ours, it is of interest that Bewilogua, after claiming in the first of the papers of reference 12 that the x-ray diffraction method is in principle a more accurate method of measuring the dimensions of gas molecules than the electron-diffraction method, retracts the statement in the second paper, which ends with the remarks that x-ray methods are the more satisfactory for the determination of electron distribution, and that electron-diffraction methods are to be preferred for the measurement of interatomic distances. Bewilogua refers to the excellent agreement between observed and calculated intensities of scattering of x-rays by chlorine molecules obtained in the investigation carried out by Richter.[19] Richter, however, assumed the band-spectral value of the interatomic distance (2.0A) to be correct, and stated only that a change of ±5 percent in this distance was not compatible with his observations.

The same value 1.83±0.02A was also reported by Wierl[1] from electron-diffraction experiments, and has since been said to have been substantiated by several groups of investigators using the electron-diffraction method.[20, 21, 22] Others found the distance to be smaller. In our early work,[23] using a film distance of 30 cm, we obtained values between 1.73 and 1.79A, the two photographs given in Table I of that paper (showing five maxima) leading to 1.788A and 1.761A, respectively. We did not have confidence in these values. and thought, in view of the work of Debye and Wierl, that the value should be larger, suggesting 1.80A as not unreasonable. Braune and Knoke[24] also obtained a smaller value, 1.78A.

In the earlier investigations only a few rings were measured (not over five), and the methods of interpretation (discussed in the following section) were often arbitrary. We feel that the value 1.760±0.005A obtained in the present investigation from photographs showing as many as ten apparent maxima and ten apparent minima is reliable to the degree given by the probable error. This value is supported by the value 1.754±0.02A reported in a preliminary communication by Cosslett and de Laszlo,[25] on the basis of their measurement of seven apparent maxima.

It is of interest that the value C–Cl = 1.760A is just the sum of the covalent radii for carbon and chlorine,[26] and is thus equal (to within 0.005A) to the average of the carbon-carbon distance in diamond, 1.542A, and the chlorine-chlorine distance in Cl_2, 1.988A.

Discussion of the Methods and Results of Other Investigators

Our experience has shown that in order that interatomic distances determined by electron-diffraction methods may be relied on to within 0.01 or 0.02A (the values then being useful in considerations regarding the electronic structure of molecules) a standardized and tested procedure for measuring and interpreting the photographs must be used. We recommend two such procedures. One of these consists in matching theoretical and observed microphotometer records over a considerable range of scattering angle, as described in Section III of this paper. The second (and more generally applicable) method is the visual method of measurement and

[17] P. Debye, L. Bewilogua and F. Ehrhardt, Phys. Zeits. **30**, 84 (1929).
[18a] P. Debye, Phys. Zeits. **30**, 524 (1929); etc.
[18b] P. Debye, Phys. Zeits. **31**, 419 (1930); L. Bewilogua, Phys. Zeits. **32**, 270 (1931); etc.
[19] H. Richter, Phys. Zeits. **33**, 587 (1932).
[20] J. Hengstenberg and L. Brú, Anales Soc. Espan. Fis. y Quim. **30**, 341, 483 (1932); **31**, 115 (1933).
[21] S. B. Hendricks, L. R. Maxwell, V. L. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933).
[22] R. W. Dornte, J. Chem. Phys. **1**, 566 (1933).
[23] L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. **19**, 68 (1933).
[24] H. Braune and S. Knoke, Zeits. f. physik. Chemie **B21**, 297 (1933).
[25] V. E. Cosslett and H. G. de Laszlo, Nature **134**, 63 (1934).
[26] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

interpretation with the use of a simplified theoretical curve.

Other investigators have used various methods without testing their accuracy and reliability. Wierl[1] obtained values of $(\sin \vartheta/2)/\lambda$ from his photographs by visual measurement. (For one substance, carbon tetrachloride, he also applied an undescribed procedure in interpreting microphotometer records.) He obtained x values either by taking the points on the complete theoretical curve lying farthest above a rather arbitrarily chosen background curve, or by using the simplified theoretical expression given in Eq. (8) of this paper. In some cases he made arbitrary changes in the x values found by these methods. We believe that in general the interatomic distances reported by Wierl as determined in the course of his important and extensive investigations are reliable to about 3 percent; for some substances (benzene, certain halogen compounds[27]) results from this laboratory agree with Wierl's to within 1 or 2 percent, for others (carbon tetrachloride, cyanogen,[28] etc.) the discrepancies are larger.[29]

Hengstenberg and Brú[20] applied methods closely similar to those of Wierl in studying acetone, formic acid, formaldehyde, methyl ether, ethyl ether, and ethyl chloride, bromide and iodide. Their results are presumably reliable to within a few percent, considerable uncertainty arising from arbitrary corrections applied to the x values.[30]

Braune and Knoke[24, 31] correlated visual measurements made by laying a scale graduated in half-millimeters on the illuminated negatives with x values obtained from the complete theoretical curve by some undescribed procedure. Although their treatment was not justified by any tests, it seems to lead to consistent results, the interatomic distances reported by them for the tetrachlorides of carbon and silicon and the hexafluorides of sulfur, selenium and tellurium agreeing with ours[23, 27] to within 2 percent.

Hendricks and co-workers[21, 32] seem to have obtained x values by a procedure similar to that used by Wierl, consisting in drawing a more or less arbitrary background curve for a complete theoretical curve (including in some cases the incoherent scattering) and selecting the points on the complete curve lying farthest above the background. (There is some uncertainty as to their exact procedure; the authors themselves make the obviously incorrect statement that they use the points of inflection of the theoretical curve.) These x values are correlated with $(\sin \vartheta/2)/\lambda$ values obtained from a similar treatment of densitometer records of the photographs. Until the accuracy of this treatment has been thoroughly tested, there is no way of estimating it except by use of the fact that it was reported by the authors[21] to lead to the value 2.98A for the Cl–Cl distance in carbon tetrachloride, a value 4 percent larger than that $2.87\pm$ found by us,[33] and also to lead to values for the I–I distances in iodine molecules and in 1,3 and 1,4-diiodo-benzene in approximate

[27] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. **56**, November (1934).

[28] L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 868 (1933).

[29] Some of Wierl's results are uncertain because of variation in his procedure. For many substances he compared visually measured ring diameters directly with x values from the simplified theoretical curve. In other cases (such as bromine) he compared visually measured ring diameters with x values from the complete theoretical curve, differing by about 5 percent with those from the simplified curve. In still other cases (ethane, ethylene, allene, acetylene) he used x values taken from the simplified curve and then corrected by an arbitrary amount. These variations in procedure indicate the necessity of formulating a standard method of interpretation and testing its accuracy.

It may be mentioned that the St. John effect, which appears clearly in our measurements and in those of Braune and Knoke for certain substances, is not indicated in Wierl's $(\sin \vartheta/2)/\lambda$ values.

[30] We have reinvestigated formic acid (Proc. Nat. Acad. Sci. **20**, 336 (1934)), finding a structure different from that of Hengstenberg and Brú.

[31] H. Braune and S. Knoke, Naturwiss. **21**, 349 (1933); Zeits. f. physik. Chemie **B23**, 163 (1933).

[32] L. R. Maxwell, V. M. Mosley and L. S. Deming, J. Chem. Phys. **2**, 331 (1934).

[33] This discrepancy between our preliminary measurements on carbon tetrachloride and those of others, including themselves, was pointed out by Hendricks and co-workers. The results of this paper (and of Cosslett and de Laszlo) show that our early measurements were not in error.

It may be mentioned that these investigators[32] make the fact that their photographs of nitrogen dioxide show no rings the basis of choice among several molecular models. Our experience has shown that when the proper experimental precautions (such as the effective condensation of the introduced gas) are not observed a substance capable of producing a photograph with well-defined apparent maxima and minima may produce photographs not showing these features. We accordingly feel that the absence of rings cannot be safely used for the determination of molecular configuration and size.

agreement with those obtained by other methods.

Dornte[22, 34] has reversed the procedure of Braune and Knoke, using the simplified theoretical curves for determining the x values and correlating them with experimental values taken by some undescribed procedure from microphotometer records. As mentioned above, Dornte's interatomic-distance value for carbon tetrachloride is 4 percent too high. We have repeated Dornte's work on carbonyl compounds, with the help of Mr. J. Y. Beach, and shall soon publish the results of the investigation.

[34] R. W. Dornte, J. Chem. Phys. **1**, 630 (1933); J. Am. Chem. Soc. **55**, 4126 (1933).

Cosslett and de Laszlo[25] in their short note on carbon tetrachloride do not describe their method in detail. They find, as we do, that the first two rings on a short-distance photograph have apparent diameters corresponding to too small values of the interatomic distances.

A preliminary note on carbon suboxide has been published by Boersch.[35]

[35] H. Boersch, Naturwiss. **22**, 172 (1934). Boersch reports a structure for carbon suboxide different from that found by us (Proc. Nat. Acad. Sci. **19**, 860 (1933)). We have calculated the theoretical curve based on his model and find pronounced disagreement with our photographs. A more complete comparison of results will be made after his detailed publication has appeared.

DECEMBER, 1934 JOURNAL OF CHEMICAL PHYSICS VOLUME 2

Raman Effect of Acetylenes. I. Methyl-, Dimethyl- and Vinyl-Acetylene

GEORGE GLOCKLER AND H. M. DAVIS,[1] *University of Minnesota*

(Received September 27, 1934)

An improved helical discharge tube containing neon and mercury with a saturated solution of sodium nitrite as filter served as a monochromatic source of radiation (4358 Hg). A mechanical filter avoided overexposure of the exciting radiation. The vibration frequencies were studied on the basis of the symmetry properties of the molecules and the usual assignments have been made. Faint rotation lines were found accompanying the C⋮C vibration in liquid dimethyl-acetylene. They are interpreted as rotation of the six hydrogen atoms around the figure axis of the molecule. The moment of inertia is $I = 10^{-39}$ g×cm². The three compounds were studied in the liquid state.

INTRODUCTION

SEVERAL new features of experimental technique have been developed and thoroughly tried and since the resulting spectrograms are of excellent quality, it seems worth while to describe them.

NE-HG DISCHARGE TUBE

The ordinary mercury arc is quite an expensive piece of apparatus and it is usually inconvenient to run it for long periods; if there are voltage variations it is liable to be extinguished. Furthermore, the arc runs hot and it is not possible to place it very near a Raman tube containing a liquefied gas. For these reasons a helical discharge tube on the principle of the usual "neon-sign" was developed and has been used in this laboratory for several years.[2] The design can best be seen from Fig. 1 (A, C and D). The helix is made of quartz, corex-D or Pyrex glass. The electrodes are made of copper or iron and are large in area so that at 6600 volts 300 milliamperes pass the tube. It contains a drop of liquid mercury and several mm of neon gas. The tube runs quite cool. One can just hold one's hand on the surface. As

[1] This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by H. M. Davis in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. For a preliminary note on methyl-acetylene see Phys. Rev. **41**, 370 (1932).

[2] R. W. Wood (J. Frank. Inst. **208**, 617 (1929)) has used a helical discharge tube containing helium. The Hanovia Chem. & Mfg. Co., manufactures lamps similar to the one discussed here. However, the tubes used in this laboratory carry a much greater current than any others described so far.

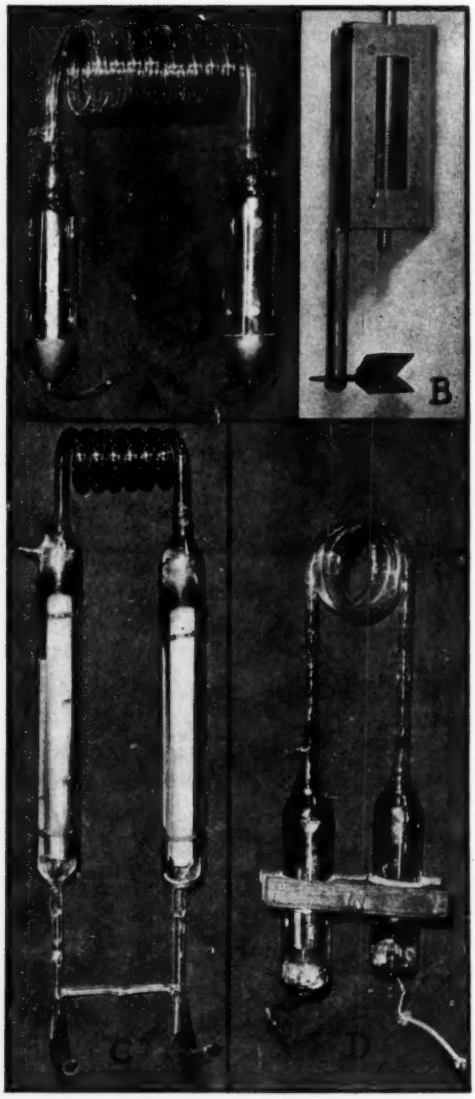


FIG. 1.

in the construction of "neon-signs" it is of great importance to out-gas the electrodes and glass-walls during the process of manufacture. One such tube has served now for 1400 hours and it is still giving good service. The area of the electrodes is determined by the rule of Claude: 1.5 dm^2 per ampere.

ELIMINATION OF OVEREXPOSURE

The exciting line for example 4358 Hg becomes greatly overexposed during the long period needed to bring out the weaker Raman lines. The unmodified line is usually completely hidden by a complete blackening of the photographic plate which may also hide some of the scattered frequencies of small wave number. In order to avoid this difficulty a mechanical filter was placed inside of the plateholder of the spectrograph in front of the photographic plate. It prevented the scattered light (4358A) from reaching the photographic plate. However, an initial exposure of about 15 minutes served to record the unmodified line. This procedure made it possible to use 4339A Hg as a reference line for the measurement of the plate. This line appeared on the spectrogram as a very sharp line and served the purpose admirably. The mechanical filter is shown in Fig. 1B and the results which can be obtained by its use are shown in Fig. 2.

PHOTOGRAPHIC PLATES

Eastman Hyper Press Plates proved most satisfactory on account of their high speed, their insensitivity in the extreme red and their high sensitivity in the blue-green. This region in the spectrum was of most interest for 4358A Hg was used as exciting radiation rather than ultraviolet light for fear that photochemical action might become troublesome with the compounds studied. The plates mentioned above proved most satisfactory for all the work except that of photographing the C–H frequency (3300 cm^{-1}) which falls in the region 5100A when excited by 4358A. Eastman spectroscopic plates, type 1-J specially sensitized for the region were found most satisfactory.

METHYL-ACETYLENE

The maximum number of vibration frequencies (f) to be expected from a molecule depends on the number of degrees of freedom which, in turn, depends on the number of atoms (N) of the molecule reduced by six (translation and rotation) $f=3N-6$.

However, this number is reduced[3,4] if the molecule has symmetry. Methyl-acetylene should

[3] C. J. Brester, *Kristall-Symmetrie und Rest-strahlen, Diss.*, Utrecht (1923) and Zeits. f. Physik **24**, 324 (1924).
[4] G. Placzek, *Leipziger Vorträge*, Verlag S. Hirzel, Leipzig (1931).

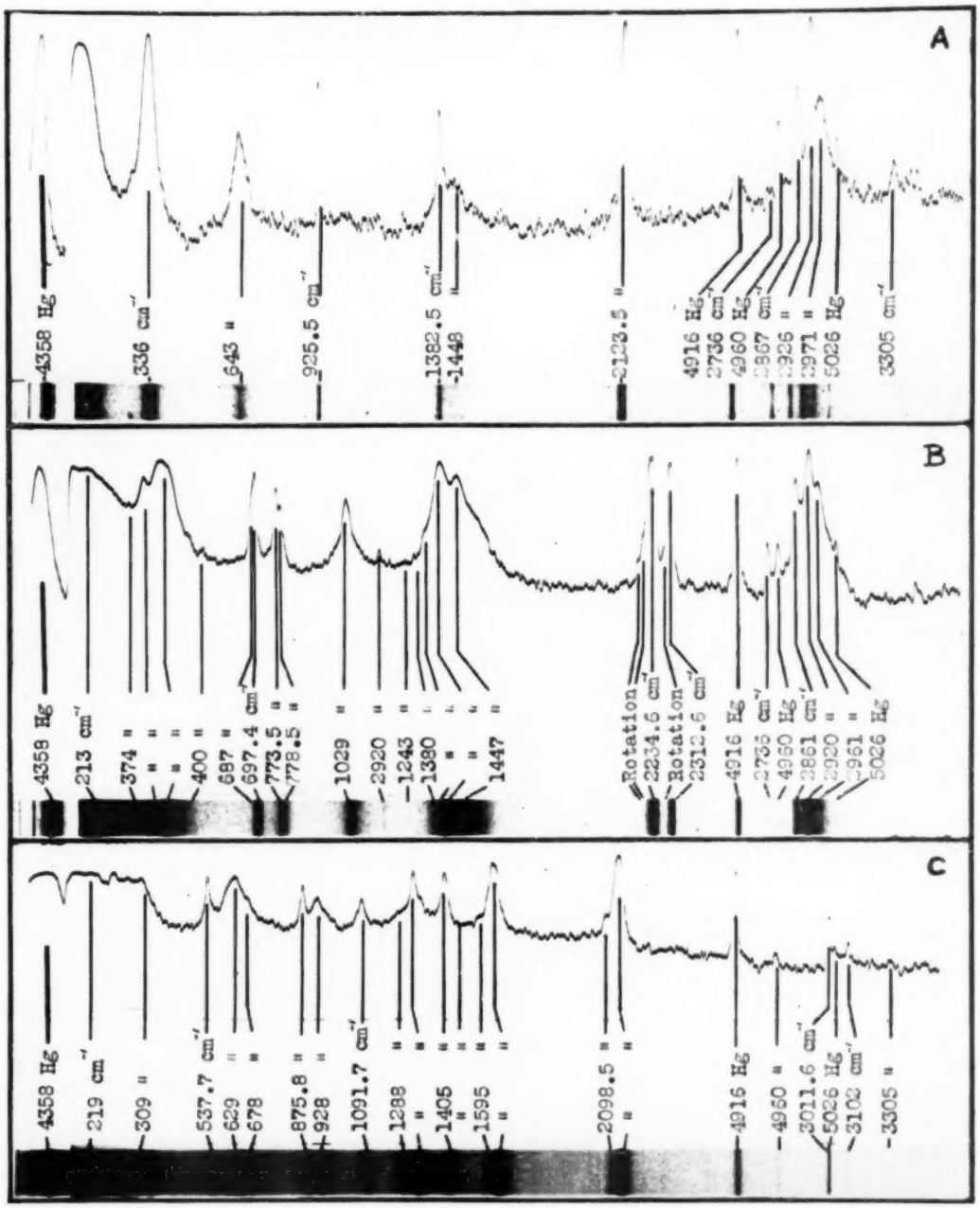


FIG. 2. Raman spectra of liquid methyl acetylene (A), dimethyl-acetylene (B) and vinyl-acetylene (C) excited by 4358 Hg.

TABLE I. *Number of vibration frequencies of methyl-acetylene.* Seven atoms; $f=7\times3-6=15$; symmetry group $=C_{3v}$.[3] (Molecular axis $=z$-axis.)

Type	Number of frequencies: Total	Zero	Net	Kind	Electric moment
A_1	2+4	1	5	active	$M(x)=M(y)=0$; $M(z)\neq0$
A_2	1	1	0	inactive	
B_1	0		0	inactive	
B_2	0		0	inactive	
C	3+4	2	5	active, double	$M(xy)\neq0$; $M(z)=0$
D	0		0		
	21	6	10		

show a maximum of 15 frequencies since it contains seven atoms. Since it, however, possesses symmetry of the type C_{3v} this number of frequencies is reduced to ten (Table I) of two groups of five each. The threefold symmetry axis of the molecule contains the three carbon atoms and the hydrogen attached to the carbon of the acetylene bond. The three hydrogen atoms of the methyl group give the molecule its threefold symmetry.

Not all of these frequencies need show up in the Raman effect or in infrared absorption. Infrared absorption is possible if the electric moment of the molecule changes during the transition and Raman lines have intensity other than zero if the polarizability of the molecule changes with changes in nuclear distances during the process of interaction with the incoming quantum.[5, 6, 7] In general this situation depends greatly upon the constitution of the molecules and upon the type of vibration involved. In other words, the ten vibrations considered may be "infrared active" and/or "Raman-active."

The results of the experimental work show that there are eleven Raman frequencies (Fig. 2 and Table II). One of them can be interpreted as an overtone and the other ten fall into two groups: five of them are very sharp lines and the five others are broad. Within the two groups the frequencies arrange themselves in inverse proportion to the reduced mass (proportional to $m_1\times m_2$) of the vibrating systems.

[5] G. Placzek, Zeits. f. Physik **70**, 84 (1931).
[6] G. Placzek and E. Teller, Zeits. f. Physik **81**, 209 (1933).
[7] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

TABLE II. *Raman-lines of methyl-acetylene.* Two types: $A_1(M(z)\neq0)$ and $C(M(xy)\neq0)$. (b=broad, s=sharp) ($\downarrow$)=perpendicular to valency bond; ($\rightarrow$) =parallel to valency bond.

Mode	cm^{-1}	Intensity	Type	μ: C	μ: A
$(H_3C)\downarrow.C\uparrow\vdots C\uparrow.H\downarrow$	336	9(b)	C	384	
$(H_3C)\downarrow.C\uparrow\vdots(CH)\downarrow$	643	5(b)	C	336	
$(H_3C)\rightarrow\cdot\leftarrow(C\vdots CH)$	929.5	8(s)	A		375
$H\uparrow.H_2\downarrow.(C.C\vdots C)\uparrow.H\downarrow$	1382.5	6(b)	C	111	
$H\uparrow.H\downarrow.(HC.C\vdots CH)$	1448	2(b)	C	76	
$(H_3C).C\rightarrow\vdots\leftarrow C.(H)$	2123.5	11(s)	A		351
2×1382.5	2736	1(b)	—		
$(H_3)\rightarrow\cdot\leftarrow(C.C\vdots C).H\rightarrow$	2867	6(s)	A		144
$(H_3)\rightarrow\cdot\leftarrow(C.C\vdots CH)$	2926.2	10(s)	A		111
$H\rightarrow\cdot\leftarrow(H_2C.C\vdots CH)$	2971	4(b)	C	39	
$(H_3C.C\vdots C)\rightarrow\cdot\leftarrow H$	3305	2(s)	A		39

Modes of vibration

336 and 643 cm^{-1}. The two lowest frequencies in methyl-acetylene are thought to be deformations[8] and to the lower frequency the larger reduced mass has been ascribed.

929.5 cm^{-1}. This frequency is in the range ascribed by Dadieu and Kohlrausch[9] to the vibration of an end methyl-group against the rest of the molecule. They trace this vibration from 990 cm^{-1} in ethane to 870 cm^{-1} in propane and 843 cm^{-1} in pentane. In the odd paraffin molecules longer than ethane the frequency appears to split into three, as in propane, 870, 940, 1050 cm^{-1}.

1382.5 cm^{-1}. It seems to depend upon the presence of a methyl-group attached to an unsaturated carbon atom. It is not present in the paraffins and frequencies in this range appear in olefines only when a CH_2 or CH_3 group is adjacent to an ethylenic carbon. In substituted acetylenes a CH_2-group next to the acetylenic carbon gives a frequency of 1320–40 cm^{-1}; but a CH_3 group so located gives always the frequency found here, i.e., 1380 cm^{-1}:

Methyl acetylene	1382.5 cm^{-1}
Dimethyl acetylene	1379.5 " [10]
Methyl, n-amyl acetylene	1384 " [11]
Methyl, phenyl "	1383 " [11]

[8] R. Mecke, Zeits. f. Elektrochemie **36**, 589 (1930).
[9] Dadieu and Kohlrausch, Ber. **63**, 273 (1930).
[10] See below.
[11] Bourguel and Daure, Bull. Soc. Chim. **47/48**, 1349 (1930).

This frequency is ascribed to a deformation involving the hydrogen atoms of the methyl group as indicated in Table II.

1448 cm^{-1}. It seems well established that this frequency occurs only when a carbon atom bearing at least two hydrogen atoms is present in the molecule. Its essential constancy found in the most different compounds indicates that it is an "inner frequency" of the CH_2 or CH_3 group. Any frequency involving the C–H binding and yet so low must be of the deformation type. It is ascribed to the transverse swing of two hydrogen atoms.[12, 13]

2123.5 cm^{-1}. All compounds containing triply bound carbons (acetylene bond) show a vibration in this immediate neighborhood. (See, however, vinyl-acetylene below.)

2736 cm^{-1}. Because of its extreme weakness and for the fact that it lies below the usual range of C–H frequencies this line is regarded not as a fundamental but as the first harmonic of 1382 cm^{-1}. Since it is slightly less than double it would indicate that the motion is anharmonic to some extent. It might be a combination tone of 2123.5 and 643 cm^{-1}. But this assignment appears improbable when it is pointed out that isobutylene shows that frequency strongly.[1] In this case the first interpretation is the only one possible.

2867, 2926.2, 2971 cm^{-1}. These frequencies are due to the motions of the hydrogen atoms. The highest one is ascribed to the motion of one hydrogen atom only along its valency direction. Of course, the remainder of the molecule moves appropriately relative to the center of gravity, although the extent of this displacement would be very small. The reduced mass involved would be smallest if one hydrogen atom only vibrates, giving rise to the largest C–H frequency. From an appropriate model it can be seen that the electric moment is most likely changed in direction perpendicular to the symmetry axis. The symmetry axis is the Z-axis and for this motion $M(z)=0$ (see Table I). Having disposed of this vibration it is possible to ascribe 2926.2 and 2867 cm^{-1} to the symmetrical and asymmetrical frequencies as they appear also in methane. It appears that the frequencies 2926.2, 2867, 1448 and 1382.5 have to one another the same relation as have the frequencies 3022, 2915, 1520, 1304 in methane.[14]

3305 cm^{-1}. The hydrogen atom attached to an acetylenic carbon atom causes this motion.

It is to be pointed out that the ten frequencies considered to be fundamentals fall into two groups as concerns their appearance and that the assignments made also follow this same division. All the sharp lines are of a character such that the change of electric moment involved is along the symmetry axis (Z-axis) and the broad, diffuse lines are of a type of motion involving changes in the moment perpendicular to the symmetry axis ($M(xy)\neq 0$; $M(z)=0$). It appears that all of the fundamental frequencies of methyl-acetylene are "Raman-active." While they have been discussed on the usual basis of vibration of certain bonds or groups, it must be stated that the molecule as a whole executes the vibration. The modes of vibration, their type, intensity and character of the lines pertaining to them agree and give a satisfactory picture of the fundamental motions of this molecule.

Dimethyl-Acetylene

The molecule contains ten atoms and should have twenty-four frequencies. Fifteen frequencies

Table III. *Number of vibration frequencies of dimethyl acetylene.* Ten atoms; $f=10\times 3-6=24$; symmetry group: D_{3h}.[3]

Type	Number of Frequencies: Total	Zero	Net	Kind	Electric moment
A_1'	2+2		4	inactive; sym.	$\Delta M=0$
A_1''	2+2	1	3	active; asym.	$M(z)\neq 0$
A_2'	1	1	0	inactive; sym.	$\Delta M=0$
A_2''	1		1	inactive; asym.	$\Delta M=0$
C'	3+2	1	4	active; sym; double	$M(xy)\neq 0$
C''	3+2	1	4	inactive; asym; double	$\Delta M=0$
	30	6	16		
				Symmetry group: S_6	
A	3+2	1	4	inactive; sym	$\Delta M=0$
B	3+2	1	4	active;	$M(z)\neq 0$
C	3+2	1	4	active; double	$M(xy)\neq 0$
D	3+2	1	4	inactive; double	$\Delta M=0$
	30	6	16		

[12] Dadieu and Kohlrausch, Ber. **63**, 262 (1930).
[13] Cross and Daniels, J. Chem. Phys. **1**, 52 (1933).
[14] R. Mecke, *Leipziger Vorträge*; Verlag von S. Hirzel, Leipzig (1931), p. 23.

TABLE IV. *Raman lines of dimethyl-acetylene.* Four types $A(\Delta M=0)$: $B(M(z)\neq 0)$; $C(M(xy)\neq 0)$; $D(\Delta M=0)$.

Mode	cm^{-1}	Intensity	Type	$m_1 \cdot m_2$	Mode	cm^{-1}	Intensity	Type	$m_1 \cdot m_2$
$H_3\uparrow.C_2\downarrow \vdots C_2\uparrow.H_3\downarrow$	213	1(*b*)	*A*	729	$H\downarrow.H\uparrow.HC.C \vdots C.CH_3$	1447	4(*b*)	*D*	104
$H_3C\downarrow.C\uparrow \vdots C\downarrow.CH_3\uparrow$	374	5(*b*)	*D*	729	Rotation	2179.45	1(*s*)	—	—
$H_3C\downarrow.C \vdots C\uparrow.CH_3\downarrow$	400	0(*b*)	*C*	720	"	2201.40	1(*s*)	—	—
$H_3C\downarrow.C.C \vdots CH_2\uparrow.H\downarrow$	687	3(*b*)	*C*	608	$H_3C\rightarrow.C\rightarrow \vdots \leftarrow C.CH_3\rightarrow$	2234.60	6(*s*)	*B*	504
$H_2C\downarrow.H\uparrow.C\downarrow \vdots C\uparrow.H\downarrow.CH_2\uparrow$	697.4	4(*s*)	*D*	729	Rotation	2280.2	1(*s*)	—	—
$H_3C\rightarrow\cdot\leftarrow C \vdots C\rightarrow\cdot\leftarrow CH_3$	773.5	4(*s*)	*A*	729	$H_3C\rightarrow.C\rightarrow \vdots \leftarrow C.\leftarrow CH_3$	2312.65	6(*s*)	*A*	729
$H_3C\rightarrow\cdot\leftarrow C \vdots C.CH_3\rightarrow$	788.5	3(*s*)	*B*	720	2×1379.5	2736.8	2.5(*s*)	—	—
$H_3C\rightarrow\cdot\leftarrow C \vdots C.CH_3$	1029	3(*s*; *b*)	*B*	585	$H_3\rightarrow\cdot\leftarrow C.C \vdots C.C.H_3\rightarrow$	2861.8	4(*s*)	*B*	288
$H_3\downarrow.C.C \vdots C.C.H_3\downarrow$	(1243)	0(*b*)	*D*	8	$H_3\rightarrow.C.C \vdots C.C.\leftarrow H_3$	2920	7(*s*)	*A*	9
$H_2\downarrow.H\uparrow.(C.C \vdots C.C)\downarrow.H\uparrow.H_2\downarrow$	1379	5(*b*)	*C*	104	$H\rightarrow.C.C \vdots C.CH_3$	2961	3.5(*b*)	*C*	53

were found which could be ascribed to vibrations. Another one appears to be an overtone. Three weak lines indicate rotation of the molecule. They accompany the acetylenic carbon atom vibrations. The number of vibration frequencies found is less than the maximum number expected, indicating that the molecule has symmetry. It, of course, has threefold symmetry on the ordinary views of organic chemistry. If the two sets of three hydrogen atoms of the methyl-groups are located exactly below one another, then the molecule has a threefold axis of symmetry, three planes of symmetry containing the threefold symmetry axis and another plane of symmetry perpendicular to the threefold axis. There are furthermore three twofold axes of symmetry perpendicular to the threefold axis. The four carbon atoms are located on the threefold axis. The symmetry group would be D_{3h} and sixteen fundamental frequencies are to be expected (Table III). The same agreement between number of fundamentals expected and Raman lines found is obtained, when it is proposed that the hydrogen atoms of the two methyl groups are not located directly below one another, but that they are displaced by 60°. The point-group is then S_6. Again sixteen fundamentals are to be expected. This number also agrees with the number of vibration lines found. In the last case the molecule contains a sixfold rotation reflection axis. The details of the expected frequencies are found in Table III. Since sixteen frequencies are expected, the attempt was made to locate another line on the Raman plates and a very weak line was found at 1243 cm^{-1}. The second arrangement of symmetry would be preferred, for, if the hydrogen atoms of the two methyl groups interact at all they would assume the puckered arrangement involved in a point system symmetrical to a rotation reflection axis. The attempt was therefore made to arrange the sixteen frequencies into four groups each. The results are shown in Table IV. Within the group *A* the first two frequencies are deformations and the lower frequency has the larger reduced mass. The same is true of the two vibration frequencies of this group. The frequencies of group *B* and *C* are also arranged in the inverse order of the reduced mass. In the fourth group *D* it is found that the reduced mass is the same for the first three frequencies. It must then be assumed that the force constant varies appropriately to account for the magnitude of the frequencies themselves. It should be noted that the Raman lines could be divided into two equal groups in regard to their appearance as sharp or broad lines. The double frequencies (*C* and *D* of S_6) could be identified with the broader lines. This division fitted quite well into the usual assignments of modes of vibration. For example, the "acetylene-bond" frequencies are relatively sharp and they fit into group *A* and *B*. It is of importance to note that the division of the Raman lines as sharp and broad was made before they were assigned into the groups shown in the tables.

Modes of vibration

213, 374 and 400 cm^{-1}. These low frequencies of dimethyl-acetylene are taken to be deformations. It should be noted that the modes of vibration assigned to various frequencies indicate in some cases only the general type of mo-

tion involved. It is possible to vary them to some extent. It seems natural to involve larger moving masses for the lower frequencies.

687 and 697.4 cm^{-1}. Because of the larger value of these frequencies, hydrogen atoms were supposed to be involved in these deformations similar to 643 cm^{-1} in methyl acetylene.

773.5, 788.5 and 1029 cm^{-1}. Since these frequencies are in the neighborhood of 990 cm^{-1} they are ascribed to the C−C bond.

1379 cm^{-1}. This frequency is ascribed to a motion similar to the one which refers to 1382.5 cm^{-1} in methyl-acetylene.

1447 cm^{-1}. It is found as 1448 cm^{-1} in methyl-acetylene.

2234.6 and 2312.6 cm^{-1}. They refer to the acetylene bond and are asymmetrical and symmetrical frequencies, respectively.

2736.8 cm^{-1}. This vibration is thought to be the overtone of 1379 cm^{-1}.

2861.8, 2920 and 2961 cm^{-1}. They refer to hydrogen atoms of the methly groups. It is to be noted that a high frequency corresponding to hydrogen attached to an acetylenic carbon atom is not found.

Rotation in dimethyl-acetylene

Three lines (2179.5, 2201.4 and 2280 cm^{-1}) are found to accompany the acetylene bond vibrations. They are interpreted as rotation changes occurring with the C ⋮ C vibration. These lines are weak requiring 97 hours exposure, but repeated measurements indicate two rotation frequencies of 33 cm^{-1} and 55 cm^{-1}. Similar rotation phenomena have been found by Bonino and Cella[15] in pinene. In this latter case the rotating portion of the molecule is a simple rotator of one degree of freedom. In the present case it is similarly assumed that the rotational energy states are given by $E_{rot}=h^2k^2/8\pi^2I=Bk^2$; $\Delta k=-2$; $\Delta\nu=B(4k-4)$ where "k" refers to the initial state. The change in k has been taken to be two units as is usual in the Raman effect. The moment of inertia calculated from the above formula appears to be connected with the rotation of the six hydrogen atoms around the figure axis of the molecule. Since the interval of 22 cm^{-1} is equal to $8B$:

$$I=h/8\pi^2cB=(27.7\times10^{-40})/2.75$$
$$=10\times10^{-40}\ \text{g}\times\text{cm}^2.$$

If it is assumed that the four carbon atoms are located on the figure axis and therefore do not contribute to the moment of inertia then the six hydrogen atoms only are responsible for this moment. Their distance from the figure axis may then be calculated:

$$6\times1.663\times10^{-24}\times r^2\times10^{-16}=10\times10^{-24};$$
$$r=1\ \text{Angstrom}.$$

Since the C–H distance in many hydrocarbons is about 1.08A, the same value may be assumed for the methyl groups of this compound. The central angle calculated is 112° instead of the usual 109° for a regular tetrahedron.

In Table V it is seen that the even rotation states only occur and that the odd ones are entirely missing. The rotation states found in Pinene by Bonino and Cella[15] are similar in character. Further, only the P branches are found in both cases. It appears that a molecule rotating in a higher quantum state due to temperature distribution of energy can interact with the scattered quantum and give up its rotation energy, while the incoming quantum cannot excite the oscillation of the acetylene bond and at the same time cause the rotation energy of the molecule to increase. This difference does not arise from the Boltzmann factor nor from the ν^4 factor in the intensity expression pertaining to Raman scattering,[16] but must arise from the

TABLE V. *Rotation in dimethyl-acetylene.*

Frequency				
No.	cm^{-1}	Δk	$\Delta\tilde{\nu}=2.75(4k-4)$	Intensity
1	(....)	2→0	11	—
2	—	3→1	22	0
3	33	4→2	33	1
4	—	5→3	44	0
5	55	6→4	55	1
6	—	7→5	66	0

[15] G. B. Bonino and P. Cella, Mem. Acad. Italia II (No. 4) 1 (1931).

[16] G. Placzek, *Rayleigh Scattering and Raman Effect*, Handb. d. Radiologie by E. Marx, Akad. Verlags-Gesellschaft m.b.H. Leipzig, 1934, p. 203.

TABLE VI. *Raman lines of vinyl-acetylene.* Two types: $A(M(x)\neq 0)$; $B(M(yz)\neq 0)$.

Mode	cm^{-1}	Intensity	Type	$m_1 \times m_2$	Mode	cm^{-1}	Intensity	Type	$m_1 \times m_2$
$(H_2C)\downarrow : (CH)\uparrow .C\downarrow \vdots CH\uparrow$	219	4(*b*)	*A*	676	$(H_2C_2)(H)\downarrow (C_2H)$	1288	4(*s*)	*A*	51
$(H_2C)\downarrow : (C_3H)\uparrow .H\downarrow$	309	4(*b*)	"	555	$H\uparrow H\downarrow (C_4H_2)$	1405	4(*s*)	*B*	100
$(H_2C)\uparrow : (C_2H)\downarrow \vdots (CH)\uparrow$	538	4(*s*)	*B*	675	$(H_2C)\rightarrow : \leftarrow (CH)(C_2H)\rightarrow$	1595	5(*s*)	"	507
$(H_2C)\downarrow : (CH)\uparrow .(C_2)\downarrow .H\uparrow$	629	4(*b*)	*A*	532	$(H_3C_2)\rightarrow C\rightarrow \vdots \leftarrow C.\leftarrow H$	2098.5	6(*s*)	"	507
$(H_2C)\downarrow : (CH)\uparrow .(C_2H)\downarrow$	678	2(*b*)	"	507	$(H_2)\rightarrow\leftarrow (C_4H_2)$	3011.6	4(*s*)	"	100
$(H_3C_2)\rightarrow .\leftarrow (C_2).(H)\rightarrow$	875	3(*s*)	*B*	672	$H\rightarrow\leftarrow (C_4H_3)$	3102	2(*s*)	"	51
$(H_3C_2)\rightarrow .\leftarrow (C_2H)$	928	2(*s*)	"	675	$(C_4H_3)\rightarrow\leftarrow H$	3305	1(*s*)	"	51
$(H_3C_2)\rightarrow C\leftarrow (CH)$	1091	2(*s*)	"	351					

difference in the expression for the scattering-tensor in the two cases.

After this research was in progress, B. Gredy[17] reported a list of Raman frequencies in dimethyl-acetylene. Of the three lines 351, 971 and 2996 cm^{-1} reported by him no trace has been found, even on exposure long enough to photograph the rotation-vibration bands mentioned above. On the other hand, he fails to report the lines at 778.5, 1029 and 2737 cm^{-1}. Since he does not mention his source of light, it is impossible to search his list for coincidence with lines of the exciting spectrum. It should be mentioned that our sample of dimethyl-acetylene was purified with extreme care; that both long and short exposures were made; that the measurements made on different plates agreed very closely and that microphotographs were made to assist in the study of the spectrum.

VINYL-ACETYLENE

The molecule contains eight atoms and eighteen fundamental frequencies may be expected. Its structure is represented by the point arrangement C_{1h} and all of the eighteen frequencies should be found, if they are "Raman-active."[4] Only fifteen frequencies could be located with certainty. The others may be coincident with mercury lines or they may be very faint. It is possible that longer exposure may reveal them, although the spectrogram shown in Fig. 1 was obtained on 25 hour exposure. The frequencies expected fall into two classes ($A=5$ and $B=13$) and the Raman lines found on the plates were divided into sharp and broad lines as is shown in Table VI.

[17] B. Gredy, Comptes rendus **197**, 327 (1933).

Modes of vibration

In some respects vinyl-acetylene is the most interesting compound studied. One can scarcely conceive of a molecule of eight atoms of only two types (carbon and hydrogen) having a greater variety of atomic bindings. One can expect to find in vinyl-acetylene almost all of the frequencies of hydrocarbon molecules. It will be noted that the organic chemists' picture of the molecule indicates (1) the presence of single, double and triple bonds between carbon atoms; (2) that the double and triple bonds are each in conjugate positions to the other; (3) that of the four hydrogen atoms three are attached to carbon atoms of distinctly different character and (4) that there are carbon atoms holding none, one and two hydrogen atoms. All of these accepted points make themselves felt in its Raman spectrum.

219 to 678 cm^{-1}. These low vibrations are considered to be due to deformations of the molecule. The assignments made are meant to indicate this situation in a general way.

As far as possible the frequencies were assigned in such a way that the masses vibrating toward one another were larger for the smaller frequencies. This point may have some significance at least within a group of vibrations involving the same bond vibration and hence the same force constant.

875, 928, 1091 cm^{-1}. These frequencies are ascribed to vibrations involving the C−C bond. The modes of vibration indicated in the table are meant to indicate the motions involved in a general way only. The types of vibration shown are to be thought of as being interchangeable among the three frequencies as no evidence exists to assign them definitely.

1288.1 cm^{-1}. This line has no counterpart in either mono-methyl or dimethyl-acetylene. Its occurrence in a Raman spectrum seems to depend upon the presence in the molecule of a lone hydrogen atom on an ethylenic carbon. This can be seen as follows: Butadiene (1277); 1-methyl-butadiene (1288); 2-methyl-butadiene (1291). However in 2–3-dimethyl-butadiene where the structure "CH" is missing, no frequency is found in the range 1024 to 1339 cm^{-1}. Again it is found in allyl alcohol (1288) and allyl sulfide (1291). The frequency reported here in vinyl-acetylene (1288.1 cm^{-1}) has also been found in divinyl-acetylene by C. E. Morrell[18] as 1288.3 cm^{-1}. Since this frequency is too low for a C–H vibration along the valency direction, it is thought to be of the deformation type.

1595 cm^{-1}. As the presence of the conjugate double bond lowers the acetylene bond frequency, so it appears that the ethylene bond frequency is also lowered by the conjugate triple bond. The frequency of the carbon-carbon double bond is ordinarily in the range of 1630–40 cm^{-1} and is thus 40 cm^{-1} lower in vinyl-acetylene.

1405 cm^{-1}. A transverse motion of the two hydrogen atoms of the CH_2 group is held responsible for this vibration.

2098.5 cm^{-1}. This vibration represents the acetylene bond vibration between the two triply-bound carbon atoms. It is lower than 2119–20 cm^{-1} found in many acetylene compounds[19] and the neighboring double bond may be responsible for this change.

3305 cm^{-1}. This frequency is due to the hydrogen atom attached to the acetylenic carbon atom.

3102 cm^{-1} is ascribed to the single hydrogen atom attached to the ethylenic carbon.

3011.6 cm^{-1} represents the vibration of the hydrogen atoms attached to the end carbon atom of the ethylene radical. The principle C–H line in ethylene itself is at 3019 cm^{-1} and is also found in many compounds having the CH_2 group.[20] It is interesting to note that the hydrogen atoms in vinyl-acetylene have a higher frequency of vibration than the hydrogen of the methyl group (Fig. 1) of methyl and dimethyl-acetylene.

It is believed that the assignments made for the motions of the molecules connecting them to certain observed frequencies is all that can be done at the present from such observations as are carried out in a scattering experiment. The symmetry of the molecules has been noted, the classes of frequencies expected have been kept in mind and the possible modes of vibration have been related to the chemical structure of the molecules.

[18] Unpublished results obtained in this laboratory.

[19] Bourgel and Daure, Comptes rendus **190**, 1298 (1930).

[20] Dadieu and Kohlrausch, references 9 and 12, pp. 322–3.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Note on "The Experimental Determination of the Heat Capacity of Explosive Gases." A Correction[1]

In a recent article[2] we outlined a method for the determination of the heat capacity of explosive gases from pressure records of explosions in a spherical vessel and have applied it to the heat capacity of ozone. Although Eq. (14) from which Cu, the heat capacity of the unburned gas mixture, was calculated, is rigidly correct, it occurred to us that the quantity, T_{be}, representing the temperature of the burned gas near the wall is not obtainable from Eq. (4) because this relationship is not an independent one. In order to calculate Cu, T_{be} must be determined in some independent way such as by direct measurement. Whether this can be done with sufficient accuracy depends on the future development of existing methods of measuring temperatures of explosions in enclosures.

The calculated values of the heat capacity of ozone must therefore be withdrawn.

BERNARD LEWIS[3]
GUENTHER VON ELBE[4]

Physical Chemistry Section,
Pittsburgh Experiment Station,
U. S. Bureau of Mines,
Pittsburgh, Pennsylvania,
November 3, 1934.

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)
[2] Lewis and von Elbe, J. Chem. Phys. 2, 291–295 (1934).
[3] Physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.
[4] Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

The Raman Spectrum of Fluorobenzene

Several months ago, we reported the results of an investigation of the Raman spectrum of fluorobenzene in this journal.[1] Three other papers have appeared within the last year which deal with this subject.[2, 3, 4] The authors of the latest of these disagree with our assignments of Raman frequencies to four observed lines, two of which were also found by them. These authors used a filter of iodine in carbon tetrachloride which served to reduce the background and prevent decomposition of the sample but did not permit an unambiguous assignment of some of the lines. Our data were obtained from two types of spectra obtained with different filters. In the first type, a filter of sodium nitrite, nitrobenzene and praseodymium nitrate was used which reduced the intensity of the violet mercury triplet to about that of the weakest observed Raman lines and gave a spectrum excited only by the blue triplet and the green line. In the second type, a strong filter of iodine in carbon tetrachloride which reduced the intensity of the blue triplet to the point where only the strongest Raman lines were excited by the 22,938 cm^{-1} mercury line. The data afforded by these two types of spectra are incompatible with the assignments preferred by Crawford and Nielsen. The lines at 21,678 and 21,515 cm^{-1} do not appear in the spectra excited by the 22,938 mercury line but only in those excited by the 24,705 line and hence must be assigned to the latter. It is suggested by Crawford and Nielsen that the lines at 23,822 and 22,436 should be assigned to 24,335–513 and 23,039–1603, respectively, rather than to 24,705–883 and 22,938–502 as we have done.[1] The first of these assignments is highly improbable inasmuch as the 24,335 mercury line is too weak to excite the 1013 Raman line which is several times stronger than the 520 line. The second of these assignments involves an error in subtraction of 1000 for a line at 22,436 excited by 23,039 and would give a Raman frequency of 603. If we assume the error was typographical and that 603 was meant, it is evident that the line at 615 should not be excited by the 23,039 line in view of the fact that the stronger Raman line at 520 is not excited by this mercury line or by the stronger line at 22,995. Furthermore, the errors in measurement assumed by these suggested assignments are greater than we should anticipate even for lines of such low intensity.

We wish to correct an error occurring in our original paper[1] on this subject. The highest Raman frequency found was 3190 as stated in the body of the table rather than 3090 as stated in the summary at the foot of the table.

We have recently examined the polarization of the Raman lines of fluorobenzene using the technique described by Duncan and Murray.[5] The results obtained are reported below using the following symbols: Strongly polarized lines, P; partially depolarized lines, p; and strongly depolarized lines, D. 244 D, 520 D, 615 D, 807 p, 883 D, 1013 P, 1159 D, 1220 p, 1601 D and 3075 P.

JOHN W. MURRAY
DONALD H. ANDREWS

Department of Chemistry,
The Johns Hopkins University,
Baltimore, Maryland,
November 12, 1934.

[1] J. W. Murray and D. H. Andrews, J. Chem. Phys. 2, 119 (1934).
[2] N. Gopala Pai, Nature 132, 968 (1933).
[3] K. W. F. Kohlrausch and A. Pongratz, Monatsh. f. Chemie 63. 427 (1933).
[4] F. W. Crawford and J. Rud Nielsen, J. Chem. Phys. 2, 567 (1934).
[5] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. 2, 636 (1934).

The Influence of D_2O and HDO on the Mutarotation of Glucose

During the past year, we have studied the kinetics of the mutarotation of α-*d*-glucose polarimetrically with sodium light at 25.00°C in heavy water mixtures of various densities, employing a 20 cm water jacketed tube of 14 cc capacity. All solutions were prepared by adding 2.5 g solid α glucose,—initial rotation 110°—, to 25 cc water which had been redistilled 3–5 times after each experiment. If the pH is maintained[1] between 4 and 6, the catalysis by H^+ and OH^- ions is not perceptible and the reaction may be ascribed entirely to the molecules H_2O, HDO and D_2O. Sufficient HCl to make the final solution 10^{-5} M was added in every experiment. The velocity constants $k=0.4343\ k'$ (min.$^{-1}$) were calculated by the Guggenheim method, and are the averaged result of 60–80 readings ($\pm 0.01°$) of the angle of rotation for each experiment. Our data (circles) are plotted in Fig. 1 against P, the mol fraction D_2O equal to $\Delta S/0.1079$. For comparison the data of previous investigators at various temperatures have been interpolated or extrapolated to 25°C, by using an energy of activation of 17,860 cal.

Our data in heavy water mixtures are distinctly lower than the preliminary values reported by Pacsu[2] and by Moelwyn-Hughes, Klar and Bonhoeffer,[3] but are in good agreement with those reported by Wynne-Jones,[4] who performed his experiments in the presence of 10^{-4} M HCl to render the basic catalysis negligible.

The deviation from linearity is striking. If we make the customary assumption that the observed velocity is the sum of the velocities due to the molecules H_2O, HDO and D_2O, we have

$$k_{obs.}=k_{H_2O}\cdot C_{H_2O}+k_{HDO}\cdot C_{HDO}+k_{D_2O}\cdot C_{D_2O};$$

where $k_{H_2O}=k^0{}_{(H_2O)}/55.34$; $k_{D_2O}=k^0{}_{D_2O}/55.15$. Assuming

TABLE I.

$S_{25}{}^{25}$	(HDO)	(D_2O)	(H_2O)	10^5 k_{HDO} calc.	10^5 k_0 calc.	10^5 $k_{obs.}$
1.0673	26.34	21.23	7.65	9.42	485	496
1.0620	27.02	18.18	10.03	9.18	521	526
1.0449	26.84	9.53	18.89	9.05	643	644
1.0436	26.32	8.46	20.49	8.66	663	654
1.0205	16.99	1.99	36.34	8.12	844	829
1.0193	16.21	1.75	37.33	7.22	855	826
1.0153	13.43	1.10	40.77	9.08	890	891
1.0121	11.00	0.69	43.65	9.46	920	925
1.0108	9.94	0.55	44.83	10.86	933	951

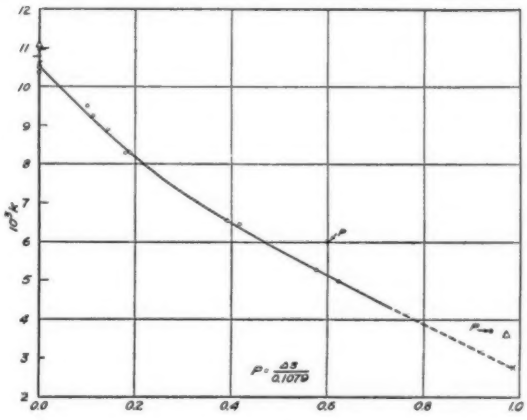


FIG. 1.

● Pacsu
△ Moelwyn-Hughes
⊖ Kilpatrick and Kilpatrick
⊸ Bronsted and Guggenheim
+ Wynne-Jones
⊕ Hudson
⊙ Hammill and La Mer (25°C)
Ordinate 10^3k
Abscissa $P=\Delta S/0.1079$

The solvent catalytic constant 10^3k as a function of P, the mol fraction of deuterium oxide at 25°C.

for the liquid state, the classical value of the equilibrium constant $K=C^2_{HDO}/C_{H_2O}\cdot C_{HD_2O}=4$, we may solve for k_{HDO}. As a result of twenty-five experiments on several preparations of α-glucose, we find $k^0{}_{H_2O}=0.01037$. With $k^0{}_{D_2O}=0.00273$ (Wynne-Jones), our calculated values of k_{HDO} are given in column 5 of Table I. The average is $k_{HDO}=9.01\times10^{-5}$ or $k^0{}_{HDO}=0.00498$. A number of experiments with 0.007 to 0.036 M HCl over the same range of D_2O indicate that $k_{(HD)+}$ the acidic catalytic constant in mixtures, is an approximately linear function of the values of k_{H^+} and k_{D^+}, as would be expected from Pedersen's recent theory of the statistical effect.[5]

W. H. HAMMILL

Department of Chemistry,
Fordham University,
New York City.

VICTOR K. LA MER

Department of Chemistry,
Columbia University,
New York City.

November 14, 1934.

[1] Nelson and Beegle, J. Am. Chem. Soc. **41**, 559 (1919).
[2] Pacsu, J. Am. Chem. Soc. **55**, 5056 (1933); **56**, 745 (1934).
[3] Moelwyn-Hughes, Klar and Bonhoeffer, Zeits. f. physik. Chemie **169**, 113 (1934).
[4] Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).
[5] Kai J. Pedersen, J. Phys. Chem. **38**, 581 (1934).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 2 NUMBER 12

DECEMBER, 1934

Published by the

AMERICAN INSTITUTE OF PHYSICS

Incorporated

LANCASTER, PA., AND NEW YORK, N. Y.

CONTENTS

J. CHEM. PHYS. 2 (1934) DECEMBER

Combination-Scattering and "Association of Molecules" . . . . . S. I. LEITMAN AND S. A. UKHOLIN 825

Formation of Negative Ions in Gases by Electron Attachment. Part I. NH_3, CO, NO, HCl and Cl_2 . . . . . NORRIS E. BRADBURY 827

Formation of Negative Ions in Gases. Part II. CO_2, N_2O, SO_2, H_2S and H_2O . . . . . NORRIS E. BRADBURY AND HOWARD E. TATEL 835

Note. Electronic Configuration of Molecules and Their Electron Affinity . . . . . NORRIS E. BRADBURY 840

X-Ray Studies of the Molecular Arrangement in Liquids . . . S. KATZOFF 841

Ultraviolet Absorption of Methane . A. B. F. DUNCAN AND JOHN P. HOWE 851

Entropy and the Absolute Rate of Chemical Reactions. I. The Steric Factor of Bimolecular Associations . O. K. RICE AND HAROLD GERSHINOWITZ 853

Theory of the Glass Electrode. III. Statistical Explanation of the Alkaline Solution Behavior . . . . . MALCOLM DOLE 862

Study of the Methods of Interpretation of Electron-Diffraction Photographs of Gas Molecules, with Results for Benzene and Carbon Tetrachloride . . . . . LINUS PAULING AND L. O. BROCKWAY 867

Raman Effect of Acetylenes. I. Methyl-, Dimethyl- and Vinyl-Acetylene . . . . . GEORGE GLOCKLER AND H. M. DAVIS 881

Letters to the Editor:

Note on "The Experimental Determination of the Heat Capacity of Explosive Gases." A Correction . . BERNARD LEWIS AND GUENTHER VON ELBE 890

Raman Spectrum of Fluorobenzene . . . . . JOHN W. MURRAY AND DONALD H. ANDREWS 890

Influence of D_2O and HDO on the Mutarotation of Glucose . . . . . W. H. HAMMILL AND VICTOR K. LA MER 891

Author Index to Volume II 892

Analytic Subject Index to Volume II 897

LANCASTER PRESS, INC., LANCASTER, PA.